III.

RESEARCHES ON THE COMPLEX INORGANIC ACIDS.

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PHOSPHO-VANADATES.

The existence of a compound of phosphoric and vanadic pentoxides appears to have been first recognized by Berzelius, who regarded it simply as a phosphate of vanadic oxide and ascribed to it the formula $V_2O_3 \,.\, 3\ P_2O_5$, vanadium being then supposed to have the atomic weight 61.5, so that its highest oxide would have the formula V_2O_3. Berzelius describes the supposed salt as lemon-yellow, crystalline, and slowly soluble in water. By dissolving together sodic phosphate and vanadate, adding nitric acid and evaporating at a gentle heat, he obtained a colorless solution which yielded a lemon-yellow salt in large grains made up of fine crystalline needles. For this compound, which he called phosphate of sodium and vanadic acid, he gave no formula. I shall endeavor to show that phosphoric and vanadic oxides unite in various proportions to form well-defined complex inorganic acids, strictly comparable with those which contain phosphoric and molybdic or tungstic oxides.

Phospho-vanadates are formed when alkaline vanadates are heated in contact with free phosphoric acid; when solutions of an alkaline phosphate are digested with vanadic acid or an acid vanadate; and when alkaline phosphates and vanadates are mixed in presence of a free acid, the conditions being, so far as I have observed, perfectly analogous to those which determine the formation of phospho-tungstates and phospho-molybdates. Phospho-vanadates of the heavy metallic oxides are formed when the divanadates of these oxides are boiled with solutions of alkaline phosphates or with phosphoric acid, and also when

the corresponding metallic phosphates are boiled with vanadic acid or acid vanadates. As a rule, the salts are beautifully crystalline, and have a yellow or orange-yellow color, passing in some cases to deep orange-red.

The general characters of the phospho-vanadates are as follows. The alkaline salts have a sulphur-yellow, and in some cases bright yellow color. They are crystalline and often present minute talcose shimmering scales. The relation of these salts to water is especially remarkable. A small quantity of water simply dissolves the phospho-vanadate with a yellow color; on adding more water, the solution gradually becomes orange, then orange-red, and finally deep red. Phosphoric acid is set free, and one or more new definite salts are formed, in which the proportion of the vanadic to the phosphoric oxide is largely increased. Precisely similar changes occur in the action of water upon arsenio-vanadates. When the deep red solutions are evaporated, the changes of color described occur again in the inverse order, and finally the original yellow salt is again obtained, though not always perfectly free from the higher compound. The facility with which the salts of this series are decomposed by water makes it often difficult to obtain them in a state of absolute purity, and renders the reactions with metallic salts uncertain as characteristics. When alkaline phospho-vanadates are evaporated with nitric acid, the base is in many cases entirely separated, and phospho-vanadic acid remains in solution and may separate in crystals. This separation of fixed base often takes place in presence of an excess of phosphoric acid alone. Solutions of alkaline phospho-vanadates appear to be partially reduced by dust or traces of organic matter with exceptional facility. In such cases the solutions take a more or less distinct greenish color, and phospho-vanadico-vanadates are formed. The solutions of these last salts are not very easily oxidized by bromine or nitric acid, and it is therefore advisable in preparing phospho-vanadates to avoid as much as possible the presence of reducing agents. Alkaline phospho-vanadates dissolve readily in hot solutions of acid tungstates and molybdates, forming orange or orange-red solutions, which yield in many cases beautiful crystalline phospho-vanadio-molybdates and phospho-vanadio-tungstates.

Analytical Methods. — The method usually adopted for the separation of vanadic and phosphoric oxides by means of ammonic chloride may be successfully applied to the analysis of the phospho-vanadates. A small excess of ammonia is to be added to the solution of the salt, which is then to be heated until it becomes colorless. In this manner

we obtain a simple mixture of phosphate and metavanadate. Ammonic chloride is then to be added, and the analysis conducted in the usual manner. This method permits the separate determination of each of the pentoxides and so far offers an advantage. On the other hand, it only applies to salts with alkaline bases. It is far more convenient, and at least equally accurate, to determine the vanadium by titrition with hypermanganate under appropriate conditions. The end reaction is usually well defined in a sufficiently dilute solution. The sum of the vanadic and phosphoric oxides may be accurately determined by precipitating the solution of the two pentoxides at a boiling heat by means of mercurous nitrate, adding mercuric oxide until a small but distinct excess is present so as to perfectly neutralize the free acid, and then boiling for a few minutes. Since the ignited mass of oxides retains mercuric oxide with some tenacity, it is best, after burning off the filter with a very free access of air, to add a weighed portion of sodic tungstate and ignite until a constant weight is obtained. When the process is carefully conducted, the fused mass contains all the phosphoric oxide and all the vanadium as pentoxide. Care should be taken to oxidize the whole of the vanadium to pentoxide as more certain. Any small quantity of dioxide present is however precipitated when an excess of mercuric oxide is present. This method applies to all salts or compounds containing oxides of phosphorus and vanadium. As regards the details of the determination of vanadium by titrition with potassic hypermanganate the following points require attention.

For the reduction of vanadic pentoxide to dioxide, it is best, after adding dilute sulphuric acid, to boil with a solution of sulphurous acid and afterward to evaporate the solution nearly, at least, to dryness upon a water bath, so as to insure a perfect reduction and at the same time to expel the last traces of sulphurous oxide. Sulphydric acid gas also readily reduces the vanadic pentoxide in presence of sulphuric acid, but there is almost always a separation of free sulphur in a state of extreme subdivision. This passes readily through the filter, and the results of the titrition are not so satisfactory as when sulphurous acid is employed as the reducing agent. The solution of vanadic dioxide should be diluted till the color is pale blue, heated to about 80°–100°, and titrated hot. In the hot solution the disappearance of the hypermanganate takes place instantly, and the end reaction is much more quickly and satisfactorily attained. The actual results are precisely the same as when a cold solution is employed, as the following titritions sufficiently prove.

I. In a cold solution of VO_2 in SO_4H_2 three successive portions of 200 cc. each required 4.62 cc., 4.64 cc., and 4.63 cc. of hypermanganate solution.

II. At 53° C. 200 cc. as before required 4.62 cc.

III.	At 62° C. 200 cc. required	4.66 cc.	Process rather more rapid.
IV.	At 70° C. " "	4.66 cc.	" " "
V.	At 80° C. " "	4.65 cc.	Color vanished instantly.
VI.	At 100° C. " "	4.64 cc.	" " "

The following analyses will show the effect of reducing by hydric sulphide, as compared with reduction by sulphurous acid. In an acid sodic vanadate: —

I.	0.0908 gr.	gave 0.0406 gr.	V_2O_5	= 44.67%	with H_2S
II.	0.1381 gr.	" 0.0607 gr.	"	= 43.92%	"
III.	0.1540 gr.	" 0.0692 gr.	"	= 44.90%	"
IV.	0.1625 gr.	" 0.0696 gr.	"	= 42.99%	with SO_3H_2
V.	0.1532 gr.	" 0.0659 gr.	"	= 43.01%	"

When hydric sulphide is used as a reducing agent, it often happens that the filtrate on evaporation deposits more sulphur. In titrating with hypermanganate, the final color reaction must be permanent for ten to fifteen minutes at least. As usual, the amount of hypermanganate required to color an equal volume of water and dilute sulphuric acid must be determined, and the proper correction applied.

In my paper on the vanadio-molybdates I have given another method of determining vanadium based upon the fact that a ferrous salt readily reduces vanadic pentoxide in the presence of free chlorhydric acid. I have since found that this method is not new, but was proposed and tested by Otto Lindemann * some years since.

1 : 1 *Ammonic Phospho-vanadate.* — When any ammonic vanadate is dissolved with an excess of ammonic phosphate, and nitric acid is cautiously added in small quantities at a time, a deep orange-red solution is obtained, which on heating becomes colorless, but which on evaporation to a small volume yields beautiful bright yellow granular crystals. These are to be carefully washed with cold water, in which they are not very soluble. The solution has at first a fine yellow color, but on continued dilution with water passes through the changes in color which have already been described. In this salt,

* Ueber die quantitative Bestimmung des Vanadins. Inaugural Dissertation von Otto Lindemann. Jena, 1879.

0.5582 gr. lost on ignition with WO_4Na_2	0.1017 gr.		= 18.22%
0.7667 gr. " " "	0.1393 gr.		= 18.17%
0.5329 gr. gave 0.0707 gr. $(NH_4)_2O$			= 13.28%
0.9753 gr. " 0.4501 gr. V_2O_5 with $KMnO_4$			= 46.15%
0.6883 gr. " 0.3174 gr. " "			= 46.13%
0.1073 gr. " 0.0495 gr. " "			= 46.15%

The analyses lead to the formula

$$P_2O_5 \cdot V_2O_5 \cdot (NH_4)_2O + aq,$$

which requires:

		Calc'd.	Mean.
P_2O_5	142	35.99	35.67
V_2O_5	182.6	46.27	46.14
$(NH_4)_2O$	52	13.17	13.28
H_2O	18	4.57	4.91
	394.6	100.00	

I have here assumed that the simplest expression of the results of the analyses represents the molecular weight. It will, I think, appear from the study of other compounds, that it is at least probable that the molecular weight is much higher. The solution of the salt is very easily reduced by dust or traces of organic matter. The solution then contains a greater or less proportion of a phospho-vanadico-vanadate. The solution of the salt has a yellow color and a very strong acid reaction, but this probably depends simply upon the decomposition which sets phosphoric acid free.

1 : 1 *Argentic Phospho-vanadate.* — A quantity of the above-described ammonium salt was dissolved with ammonic phosphate, and argentic nitrate added to the solution in excess. A sulphur-yellow crystalline precipitate was at once formed, which was digested with very dilute nitric acid so as to remove argentic phosphate, and then presented granular yellow crystals but slightly soluble in cold or hot water. The salt is readily decomposed by dilute chlorhydric acid, and then yields a yellow solution which is probably the acid of the series. In the silver salt,

1.4134 gr. gave 0.9192 gr. AgCl	= 52.59%	Ag_2O
1.6267 gr. " 0.7938 gr. metallic silver	= 52.41%	"
1.3696 gr. " 0.2851 gr. V_2O_5	= 20.82%	
1.0193 gr. lost on ignition 0.1067 gr.	= 10.47%	

The analyses lead to the formula

$$P_2O_5 . V_2O_5 . 2\,Ag_2O + 5\,aq,$$

which requires:

		Calc'd.	Found.	
P_2O_5	142	16.19		16.21
V_2O_5	182.6	20.83	20.82	
$2\,Ag_2O$	464	52.70	52.59	52.41
$5\,H_2O$	90	10.28	10.47	
	478.6	100.00		

6 : 4 *Potassic Phospho-vanadate.* — When ammonio-magnesic phosphate, $P_2O_8Mg_2(NH_4)_2$, is boiled with a strong solution of potassic divanadate, the phosphate disappears and is replaced by yellow granular masses, which are but slightly soluble in water. In this salt, after washing with cold water,

0.5401 gr. gave 0.3852 gr. P_2O_5 and V_2O_5 = 71.31%

$\begin{cases} \text{0.3790 gr. " 0.1777 gr. } V_2O_5 \text{ with } KMnO_4 = 46.89\% \\ \text{0.3790 gr. lost on ignition (alone) 0.0619 gr.} = 16.31\% \end{cases}$

The analyses lead to the formula

$$4\,P_2O_5 . 6\,V_2O_5 . 3\,K_2O + 21\,aq,$$

which requires:

		Calc'd.		Found.	
$4\,P_2O_5$	568	24.41	71.59	24.42	71.31
$6\,V_2O_5$	1098	47.18		46.89	
$3\,K_2O$	283	12.16	28.41	12.38	28.69
$21\,H_2O$	378	16.25		16.31	
	2327	100.00			

No magnesium and no ammonium could be detected in the salt, and it seems at least probable that the salts of the series might be prepared by the same process, other acid vanadates being substituted for the potassic salt employed. A strong solution in cold water gave a brick-red fine granular precipitate with argentic nitrate, and yellow flocky precipitates with mercurous and thallous nitrates. The mercurous precipitate was distinctly seen to contain two different compounds, and it is therefore probable that the potassic salt was decomposed even by a small quantity of cold water.

7 : 6 *Hydric Phospho-vanadate.* — When a solution of phosphoric acid is mixed with a strong solution of sodic divanadate, a yellow uncrystalline mass is formed. This after standing some days becomes distinctly crystalline, and may be washed with cold water until the washings become orange-red. In a preparation of this salt, dried as usual upon woollen paper,

1.2172 gr. gave 0.4846 gr. V_2O_5 = 39.81%
0.8553 gr. " 0.6487 gr. mixed oxides = 75.84% $P_2O_5 + V_2O_5$
0.6127 gr. lost with WO_4Na_2 0.1470 gr. = 24.00% water.

The analyses show that the compound analyzed contained no soda, and that it is a 7 : 6 phospho-vanadic acid, the formula of which may be written

$$7\ P_2O_5 \cdot 6\ V_2O_5 \cdot 3\ H_2O + 34\ aq.$$

The formula requires :

		Calc'd.		Found.	
7 P_2O_5	994	39.76	75.83	39.81	75.84
6 V_2O_5	1096	36.07		36.03	
37 H_2O	666	24.17		24.00	
	2756	100.00			

The sum of the phosphoric and vanadic oxides found by difference is 76.00. After all saline matters are washed out, the acid dissolves readily in water, and gives an orange solution, which changes color on dilution in the manner already explained. I shall, after describing the phospho-vanadico-vanadates and arsenio-vanadico-vanadates, return to this and the preceding compounds.

20 : 1 *Phospho-vanadic Acid.* — When a solution of phosphoric acid is mixed with one of ammonic metavanadate, the liquid becomes orange, but after heating for a time upon a water-bath lemon-yellow, and then deposits a large quantity of a lemon-yellow crystalline salt. More of this salt is deposited on evaporating the mother liquor, and again after partially neutralizing with ammonia. The yellow salt may be drained with the filter-pump and then washed with a small quantity of cold water. The salt presents fine yellow crystals which dissolve in a small quantity of hot water. The liquid is at first yellow, but on adding more hot water, and especially on heating, it becomes orange; with more water, orange-red, and finally deep garnet-red with a very strong acid reaction. If this solution is evaporated upon a water-bath the changes of color occur in the inverse order; that is to say, the liquid

gradually becomes orange-red, orange, and yellow, and the original salt is finally deposited. The changes of color observed are due to the decomposition of the ammonium salt by water, and the formation of ammonic phosphates and of phospho-vanadates differing in constitution from the original compound and containing a greater proportion of vanadic pentoxide for one molecule of phosphoric oxide. Phosphoric acid is also set free in the reaction. The deep red solution, on standing, deposits beautiful small granular ruby or garnet-red crystals. Of these crystals,

$$\begin{cases} 0.3156 \text{ gr. lost on ignition (alone) } 0.0691 \text{ gr.} = 21.89\% \\ 0.3156 \text{ gr. gave with } KMnO_4 \quad 0.2377 \text{ gr.} = 75.32\% \end{cases}$$

The analyses correspond with the formula

$$20\, V_2O_5 \,.\, P_2O_5 \,.\, 6\, H_2O + 53 \text{ aq},$$

which requires:

		Calc'd.	Found.
$20\, V_2O_5$	3660	75.24	75.32
P_2O_5	142	2.92	2.79
$59\, H_2O$	1062	21.84	21.89
	4864	100.00	

The phosphoric oxide was determined by the difference. The solution of the acid has a dark red color and a strongly acid reaction. It gives cinnamon-colored flocky precipitates with nitrates of silver and thallium. The silver salt is readily decomposed by potassic chloride in presence of a trace of chlorhydric acid, giving a red solution which deposits beautiful square thin tabular crystals, the red color of which is so deep that they appear black by reflected light. In preparing the salts of this series it will probably be best to saturate a small proportion of the acid with an alkaline base, and then to add the rest of the acid. For the present the basicity of the acid is undetermined, and the assumption that it contains six molecules of water is merely provisional. It also appears probable that salts of this and similar higher series may be prepared by mixing solutions of alkaline metavanadates with those of alkaline phosphates in definite proportions, and then adding dilute sulphuric acid in small portions at a time, stirring or shaking after each addition of acid. The precise quantity of acid to be added should be calculated beforehand, which may of course be easily done if we assume a definite basicity, as, for instance, that each molecule of salt shall contain three molecules of fixed base.

PHOSPHO-DIVANADATES.

The salts of this series are formed under conditions which have already been pointed out. They have frequently, at least, a fine yellow color, and are decomposed by water with formation of salts of other series.

Phospho-divanadate of Ammonium. — This is the yellow crystalline salt referred to as formed by the action of phosphoric acid upon ammonic metavanadate. The salt dissolves in a small quantity of cold water without apparent decomposition, but the reactions of the solution are at best rather uncertain. Argentic nitrate gives a fine bright yellow crystalline precipitate. In the ammonium salt,

1.1259 gr. lost on ignition 0.2876 gr. = 25.54% NH_3 and H_2O
1.0600 gr. " " with WO_4Na_2 0.2723 gr. = 25.69%
1.0624 gr. gave 0.1676 gr. NH_4Cl = 7.67% $(NH_4)_2O$
1.4112 gr. " 0.7534 gr. V_2O_5 = 53.40%

The analyses lead to the formula

$$P_2O_5 \cdot 2\,V_2O_5 \cdot (NH_4)_2O \cdot 2\,H_2O + 5\text{ aq},$$

which requires:

		Calc'd.	Found.
P_2O_5	142	20.74	20.98 (diff.)
$2\,V_2O_5$	365	53.28	53.40
$(NH_4)_2O$	52	7.59	7.67
$7\,H_2O$	126	18.39	17.95
	685	100.00	

The formula given corresponds to the provisional assumption of three molecules of water in the acid.

ARSENIO-VANADATES.

These salts are formed under precisely the same conditions as those which determine the formation of phospho-vanadates. The general characters of the salts are almost precisely similar. Like the phosphorus compounds, they are yellow or orange-yellow and crystalline. They are decomposed by water, and yield deep orange-red salts of new series, in which the proportion of vanadic to phosphoric oxide is largely increased.

Analytical Methods. — Arsenic is most conveniently determined in these salts by reduction with sulphurous acid and precipitation of arsenious sulphide by sulphydric acid. The sulphide is then to be weighed upon an asbestos filter. In the filtrate which contains the vanadium as dioxide the vanadic pentoxide may be determined by potassic hypermanganate. Dilute sulphuric acid is to be added in place of chlorhydric acid before precipitation with sulphydric acid. Water cannot be accurately determined in these salts by ignition with sodic tungstate, as a greater or less quantity of arsenic oxide is always volatilized. The best method consists in cautiously heating the salt over a radiating cup of sheet-iron until a constant weight is obtained.

5 : 8 *Arsenio-vanadic Acid.* — When sodic divanadate and arsenate are dissolved together in boiling water, and nitric acid is added in small portions at a time, a deep orange liquid is obtained which on evaporation to dryness upon a water-bath yields an orange-yellow crystalline mass. This is to be purified by careful washing with cold water, when a beautiful crystalline orange-colored salt remains. The salt is somewhat soluble in cold, and readily in hot water. The solution is very easily reduced by dust or other organic matters, and becomes greenish-orange with formation of a greater or less quantity of an arsenio-vanadico-vanadate. It is then difficult to reoxidize the solution so as to obtain the original compound. On analysis,

$$\left\{\begin{array}{l} 0.8558 \text{ gr. gave } 0.3374 \text{ gr. } As_2S_3 = 36.87\%\ As_2O_5 \\ 0.8558 \text{ gr. " } 0.4058 \text{ gr. } V_2O_5 \text{ with } KMnO_4 = 47.41\% \end{array}\right.$$
$$0.8715 \text{ gr. lost over a radiator } 0.1358 \text{ gr.} = 15.58\%$$

The analyses correspond to the formula

$$5\ As_2O_5 \,.\, 8\ V_2O_5 \,.\, 3\ H_2O + 24\ aq,$$

which requires:

		Calc'd.		Found.	
5 As_2O_5	1150	47.18	84.31	47.41	84.28
8 V_2O_5	1461	37.13		36.87	
27 H_2O	486	15.69		15.58	
	3097	100.00		99.86	

The water, as estimated by difference, amounts to 15.72, so that the direct determination is nearly correct, and no fixed base is present. In a second preparation, in which I employed residues containing arsenic and vanadium from the preparation of the arsenio-vanadico-vanadates

to be described and oxidized with nitric acid and potassic hypermanganate, I found the ratio of the arsenic to the vanadic oxide to be as 7 : 6.

$$\begin{cases} 1.2105 \text{ gr. gave } 0.5825 \text{ gr. } As_2S_3 = 44.99\% \ As_2O_5 \\ 1.2105 \text{ gr. } \quad \text{"} \quad 0.3748 \text{ gr. } V_2O_5 = 30.97\% \end{cases}$$

The difference here cannot be taken as water, as some manganous oxide was present; but the acid may, like the corresponding phosphorus compound, be regarded as

$$7\ As_2O_5 \,.\, 6\ V_2O_5 \,.\, 3\ H_2O.$$

Since the publication of the preliminary notice in which I announced the discovery of this class of compounds,* and threw the whole subject open to chemists, a short paper has appeared by F. Fernandez,† in which the writer describes an arsenio-vanadate of ammonium, which, except so far as water of crystallization is concerned, corresponds to the ammonic phospho-vanadate which I have described, so that we now have

$$P_2O_5 \,.\, V_2O_5 \,.\, (NH_4)_2O + aq,$$
$$As_2O_5 \,.\, V_2O_5 \,.\, (NH_4)_2O + 11\ aq.$$

Want of material has prevented a more complete study of the subject on my own part.

PHOSPHO-VANADICO-VANADATES.

The salts of this series are very readily formed by boiling an excess of a mixture of vanadic dioxide and pentoxide with alkaline phosphates, when the mixed oxides dissolve to form red or greenish-red solutions, which on cooling yield in many instances very beautiful crystalline salts. The same result is obtained by fusing the mixture of oxides obtained by igniting ammonic metavanadate with alkaline phosphates; by partially reducing phospho-vanadates, or by adding solutions of vanadic dioxide to solutions of phospho-vanadates. The alkaline phospho-vanadico-vanadates are often very beautiful, and present extremely well-defined crystals. They have usually a green color, which may be so deep as to appear black in large crystals. By oxidation they pass into phospho-vanadates.

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* American Chemical Journal, iv. 577.

† Berichte der Deutschen Chem. Gesellschaft, xvii. 1632. July, 1884.

Analytical Methods. — These are the same as those described for the analysis of phospho-vanadates. The vanadic dioxide may be determined directly by titrition with potassic hypermanganate in dilute solutions containing free sulphuric acid. In another portion of the solutions the vanadic pentoxide is to be reduced with sulphurous acid, and then determined by titrition. The whole quantity of oxides may be found by mercurous nitrate and mercuric oxide after completely oxidizing the vanadic dioxide with nitric acid.

18 : 1 : 2 *Phospho-vanadico-vanadates of Ammonium.* — When a solution of phospho-vanadate of ammonium is mixed with one of vanadic dioxide in chlorhydric acid, and the liquid is allowed to stand for some time, beautiful deep green prismatic crystals are deposited. These dissolve in hot water to a very deep red solution, and appear to be decomposed exactly in the manner which has been explained in the case of the phospho-vanadates. Of this salt,

0.3647 gr.	lost on ignition with WO_4Na_2	0.0938 gr.	= 25.72%
0.5318 gr.	gave	0.3657 gr. V_2O_5 and P_2O_5	= 68.76%
{ 0.4958 gr.	"	0.0084 gr. VO_2 with $KMnO_4$	= 1.68%
{ 0.4958 gr.	"	0.0083 gr. VO_2 with iodine and CO_3NaH	= 1.69%
0.4284 gr.	"	0.0325 gr. $(NH_4)_2O$	= 7.59%

The vanadic dioxide was oxidized with nitric acid before precipitation with mercurous nitrate and mercuric oxide. The resulting percentage is to be corrected accordingly. The analyses correspond fairly well with the formula

$$18\ V_2O_5 \cdot VO_2 \cdot 2\ P_2O_5 \cdot 7\ (NH_4)_2O + 50\ aq,$$

which requires :

		Calc'd	Found.	
18 V_2O_5	3294	66.88	67.08	
VO_2	83	1.69	1.68	1.74
2 P_2O_5	284	5.77	5.51	
7 $(NH_4)_2O$	364	7.39	7.59	
50 H_2O	900	18.27	18.13	
	4925	100.00		

The phosphoric oxide is determined by difference only. The compound may also be regarded as a double salt ; as, for instance,

$$6\ V_2O_5 \cdot VO_2 \cdot 3\ (NH_4)_2O + 2\ \{6\ V_2O_5 \cdot P_2O_5 \cdot 2\ (NH_4)_2O \cdot H_2O\} + 48\ aq\ ;$$

but we have at present no data for deciding the question. The solution in cold water gives brown flocky precipitates with salts of silver and thallium and with mercurous nitrate, none with baric chloride at first, but after a short time the mixture becomes turbid and then deposits distinct orange crystals mixed with a brown flocky matter. The salt is therefore probably decomposed by solution.

4 : 5 : 1 *Phospho-vanadico-vanadate of Sodium.* — A boiling solution of sodic orthophosphate dissolves the mixture of vanadic oxides obtained by igniting ammonic metavanadate, and gives a greenish liquid which on cooling deposits green crystalline scales with a talcose lustre. The same salt is formed by fusing together the mixed oxides and sodic phosphate, but is in this way more difficult to obtain in a state of purity. The compound is insoluble in water, and cannot therefore be purified by recrystallization. Of this salt,

1.4264 gr. lost on ignition 0.3904 gr. = 27.37% water
1.2893 gr. gave 0.8136 gr. $V_2O_5 + P_2O_5$ = 63.10%
1.7149 gr. " 0.5815 gr. V_2O_5 by titrition with $KMnO_4$ = 33.90%
1.4190 gr. " 33.67% and 33.75%

The analyses correspond tolerably well with the formula

$$5\ P_2O_5 \ .\ 4\ V_2O_5 \ .\ VO_2 \ .\ 4\ Na_2O + 37\ aq,$$

which requires:

		Calc'd.	Found.	
5 P_2O_5	710	29.11	29.15	29.32 (diff.)
4 V_2O_5	732	30.01	30.66	
VO_2	83	3.40	3.11	
4 Na_2O	248	10.17	9.74	
37 H_2O	666	27.31	27.17	
	2439	100.00		

12 : 12 : 6 *Potassic Phospho-vanadico-vanadate.* — When solutions of potassic divanadate and potassic orthophosphate, PO_4K_2H, are heated together, the phosphate being in large excess, a colorless solution is formed. A solution of vanadic dioxide in a large excess of chlorhydric acid then often produces almost immediately a precipitate of black granular crystals. In some cases, however, the black salt is formed only after standing some hours. Under the microscope the black crystals appear to be cubes, though this is rather uncertain. The true color is deep green. The salt is insoluble in water contain-

ing other saline bodies; but as soon as the crystals are completely washed, they dissolve readily in hot water with decomposition, a beautiful green salt crystallizing from the solution on standing. Of the black crystals,

0.4978 gr. lost with WO_4Na_2 0.0716 gr.		$= 14.38\ H_2O$
0.1622 gr. gave with $KMnO_4$ 0.03177 gr.	VO_2	$= 19.59\%$
0.1201 gr. " " 0.02384 gr.	"	$= 19.84\%$
0.1383 gr. " " 0.06032 gr.	V_2O_5	$= 43.62\%$
0.1360 gr. " " 0.05892 gr.	"	$= 43.32\%$
0.5646 gr. gave 0.3035 gr. $P_2O_7Mg_2$		$= 34.38\%\ P_2O_5$
0.7186 gr. " 0.3876 gr. "		$= 34.49\%$ "

The analyses lead to the formula

$$12\ P_2O_5 \,.\, 12\ VO_2 \,.\, 6\ V_2O_5 \,.\, 5\ K_2O + 40\ aq,$$

which requires:

		Calc'd.	Found.	
12 P_2O_5	1704	34.14	34.38	34.49
12 VO_2	999	20.02	19.84	19.59
6 V_2O_5	1096	21.96	22.02	22.72
5 K_2O	472	9.46	9.11	
40 H_2O	720	14.42	14.38	
	4991	100.00		

The sum of the three oxides $P_2O_5 + VO_2 + V_2O_5 = 76.12$, as calculated from the formula, and 76.51 as found from the mean of all the analyses. The analyses are very difficult, partly because no perfectly satisfactory method of separating phosphoric oxide from the other oxides has yet been found, and partly because in titrating vanadic dioxide by potassic hypermanganate the end reaction varies with the quantity of phosphoric oxide present. It is true that this variation is usually within narrow limits, but it is sometimes sufficient to affect the result by as much as 0.50%.

The beautiful crystalline green salt which is formed when the black salt above described is dissolved in hot water was also analyzed.

0.5918 gr. gave 0.3771 gr. $PtCl_6K_2$		$= 12.37\%\ K_2O$
0.4766 gr. lost with WO_4Na_2 0.0718 gr.		$= 15.06\%$
0.1617 gr. gave with $KMnO_4$ 0.03405 gr.	VO_2	$= 21.06\%$
0.1274 gr. " " 0.02708 gr.	"	$= 21.26\%$

0.0840 gr. gave with $KMnO_4$		0.01778 gr. VO_2		= 21.16%
0.1532 gr.	"	"	0.0659 gr. V_2O_5	= 43.01%
0.1612 gr.	"	"	0.0689 gr. "	= 42.77%
0.1625 gr.	"	"	0.0699 gr. "	= 42.99%

In the determination of the water by fusion with sodic tungstate, the vanadic dioxide is oxidized to pentoxide. Hence it is necessary to add to the percentage of water found — 15.06 — the percentage of oxygen required to convert 21.16% (mean) of VO_2 to the equivalent quantity of V_2O_5 or 2.03%. This correction was not applied in the case of the first salt described above, because after a rapid fusion the vanadic dioxide appeared not to have been oxidized. In determining the vanadic pentoxide in these salts the oxide is first reduced to VO_2 by boiling with sulphurous acid and then titrated with hypermanganate. From want of material the phosphoric oxide in the green salt was determined by difference only.

The analyses of the green salt correspond with the formula

$$12\ P_2O_5 \,.\, 14\ VO_2 \,.\, 6\ V_2O_5 \,.\, 7\ K_2O + 52\ aq,$$

which requires:

		Calc'd.	Mean.			
12 P_2O_5	1704	30.63	29.65 (diff.)			
14 VO_2	1166	20.96	21.16	21.06	21.26	21.16
6 V_2O_5	1096	19.71	19.73	19.82	19.80	19.58
7 K_2O	661	11.88	12.37		12.37	
52 H_2O	936	16.82	17.09		17.09	
	5563	100.00				

In this class of compounds I found it impossible to determine the sum of the acid-forming oxides by precipitating directly with mercurous nitrate and mercuric oxide. The results of many trials varied within very wide limits. Both the black and green salts are oxidized when heated with nitric acid and evaporated to degrees. Yellow crystalline masses remain, which contain phospho-vanadates, and which deserve a careful study as furnishing a new and perhaps better mode of forming that class of salts.

14 : 16 : 6 *Ammonic Phospho-vanadico-vanadate.* — When ammonic metavanadate or divanadate is boiled with a solution of ammonic orthophosphate in large excess, a colorless liquid is formed, which gives, with a solution of vanadic dioxide in chlorhydric acid, after a time, beautiful black or rather intensely deep green crystals, exactly resembling those of the potassic salt already described. The crystals

dissolve easily in hot water free from saline matter, but do not crystallize readily from the solution. Of this salt, after careful washing and drying only,

0.7744 gr. lost with WO_4Na_2 0.1859 gr. $=$ 24.01% $NH_3 + H_2O$. The oxygen gained by the vanadic dioxide is 2.14% and 24.01 + 2.14 $=$ 26.15% $NH_3 + H_2O$
0.5556 gr. gave when heated in a combustion tube 0.1451 gr. $=$ 26.11% $NH_3 + H_2O$
0.8969 gr. gave with $KMnO_4$ 0.2001 gr. $VO_2 =$ 22.31%
0.2018 gr. " " 0.0444 gr. " $=$ 22.19%
0.5626 gr. after reduction with SO_3H_2 gave with $KMnO_4$ 0.2427 gr. $=$ 43.13% V_2O_5
0.2494 gr. after reduction with SO_3H_2 gave with $KMnO_4$ 0.1067 gr. $=$ 42.76% V_2O_5
0.5325 gr. gave 0.0326 gr. $(NH_4)_2O =$ 6.13%
0.5053 gr. " 0.0309 gr. " $=$ 6.12%

The mean of the two determinations of VO_2 is 22.25%, and the equivalent in V_2O_5 24.38%, which, subtracted from 42.76 and 43.13 respectively gives 18.38 and 18.75 for the percentages of V_2O_5.

The analyses correspond closely with the formula

$$14\ P_2O_5 \,.\, 16\ VO_2 \,.\, 6\ V_2O_5 \,.\, 7(NH_4)_2O + 67\ aq,$$

which requires:

		Calc'd.	Found.	
14 P_2O_5	1988	33.21	33.06 (diff.)	
16 VO_2	1333	22.26	22.31	22.19
6 V_2O_5	1096	18.30	18.38	18.75
7 $(NH_4)_2O$	364	6.08	6.12	6.13
67 H_2O	1206	20.15	20.01	
	5987	100.00		

A portion of the very dark green salt was boiled with water, and the deep green solution allowed to stand, when much lighter green crystals separated. These were again dissolved and recrystallized. The crystals had a peculiar rusty olive-green surface color. Of this salt,

0.4770 gr. gave 0.1013 gr. V_2O_5 by $KMnO_4 =$ 21.21% and 0.1014 gr. $VO_2 =$ 21.22%
0.4014 gr. gave 0.0249 gr. $(NH_4)_2O =$ 6.20%
0.3062 gr. lost with WO_4Na_2 0.0663 gr. $=$ 21.65%

The determination of the sum of the water and ammonia must in this case be corrected for the oxygen required to convert the 21.22% of vanadic dioxide into vanadic pentoxide, since the ignition was continued with free access of air until the weight of the mass became constant. The correction is of course to be added, so that we have for the total loss 21.65 + 2.03 = 23.68%.

The analyses correspond tolerably well only with the formula

$$10\ P_2O_5 \,.\, 11\ VO_2 \,.\, 5\ V_2O_5 \,.\, 5\ (NH_4)_2O + 41\ aq,$$

which requires:

		Calc'd.		Found.	
10 P_2O_5	1420	33.44	76.50	33.89	(diff.) 76.32
11 VO_2	916	21.57		21.21	
5 V_2O_5	913	21.49		21.22	
5 $(NH_4)_2O$	260	6.12	23.50	6.20	23.68
41 H_2O	738	17.38		17.48	
	4247	100.00			

As the number of molecules of vanadic dioxide in this salt is uneven, it will be necessary to double the formula in order to obtain a symmetrical structural scheme.

ARSENIO-VANADICO-VANADATES.

The salts of this series are formed with great ease by mixing solutions of alkaline arsenates and vanadates, and adding a solution of vanadic dioxide in excess of chlorhydric acid. On evaporation large very dark green crystals are deposited in abundance. In preparing arsenio-vanadates it is difficult to avoid a partial reduction of the vanadic pentoxide by dust or other organic matter, and as a rule solutions are obtained which contain both classes of salts. The arsenio-vanadico-vanadates form a very beautiful and well-defined class of salts.

Analytical Methods. — Vanadic dioxide may be determined directly by titrition with hypermanganate after addition of sulphuric acid and appropriate dilution. To determine the arsenic present as arsenic pentoxide, the arsenic is first to be brought into the form of arsenous oxide by means of sulphurous acid after adding a little sulphuric acid to the solution. The arsenic may then be precipitated as sulphide by means of sulphydric acid, and weighed on a Gooch filter. The filtrate contains all the vanadium in the form of dioxide, which may then be determined by means of hypermanganate. The relation between the two oxides of vanadium is then easily found. The accurate determination

of the water of crystallization in these salts is difficult. They all lose arsenic oxide when heated with sodic tungstate, and the only method which can be safely employed consists in heating weighed portions over a radiating cup of sheet-iron until a constant weight is obtained.

12 : 12 : 6 *Ammonium Salt.* — When ammonic metavanadate or divanadate is boiled with a large excess of ammonic arsenate, a colorless solution is formed. On adding a solution of vanadic dioxide in chlorhydric acid, a dark blue precipitate is formed, which dissolves readily in an excess of dilute chlorhydric acid. No precipitate is formed if the solution of the dioxide contains enough free acid. After standing some hours, a very dark green, almost black, crystalline salt is deposited in quantity. This is to be washed with cold water. The crystals exactly resemble those of the black potassic phospho-vanadico-vanadate already described. They are insoluble in saline solutions, and but slightly soluble in cold water. The solution has a greenish-yellow color. It gives a brick-red indistinctly crystalline precipitate with argentic nitrate, and a dull yellow flocky precipitate with mercurous nitrate. This last becomes crystalline on standing. It will serve to prepare other salts of this series by double decomposition with chlorides. The solution of the salt gives no precipitate with cupric sulphate or baric chloride. In this salt,

1.1623 gr. gave with $KMnO_4$	0.2199 gr. VO_2		= 18.91%
0.8719 gr. " "		0.3605 gr. V_2O_5	= 41.37%
0.9726 gr. gave	0.5500 gr. As_2S_3		= 52.87%
0.8246 gr. "	0.4646 gr. "		= 52.68%
1.0209 gr. "	0.0538 gr. $(NH_4)_2O$		= 5.27%

The vanadic pentoxide, after deducting the equivalent of the dioxide found, is 20.65%. The water could not be determined either by heating with sodic tungstate or in a combustion tube, as arsenous oxide sublimed in each case. It is therefore estimated by difference.

The analyses agree fairly well with the formula

$$12\ As_2O_5 \,.\, 12\ VO_2 \,.\, 6\ V_2O_5 \,.\, 5\ (NH_4)_2O + 7\ aq,$$

which requires:

		Calc'd.	Found.	
12 As_2O_5	2760	52.65	52.68	52.87
12 VO_2	1000	19.08	18.91	
6 V_2O_5	1096	20.91	20.65	
5 $(NH_4)_2O$	260	4.96	5.27	
7 H_2O	126	2.40	2.40	
	5242	100.00		

It will be observed that this salt may be considered as derived from twelve molecules of an arsenio-vanadate by reduction of one half the vanadic pentoxide to dioxide and loss of seven molecules of ammonic oxide, since we have

$$12\ \{As_2O_5 \cdot V_2O_5 \cdot (NH_4)_2O\} =$$
$$12\ As_2O_5 \cdot 12\ VO_2 \cdot 6\ V_2O_5 \cdot 5\ (NH_4)_2O + 7\ (NH_4)_2O + 6\ O.$$

This relation might be made available in the preparation of the salt. Boiling water instantly decomposes this compound, and gives a deep green solution, which on standing deposits crystals of a peculiar deep olive-green color with a tinge of brown. The black salt corresponds exactly in composition to a phosphorus compound above described, except only as regards water of crystallization:

$$12\ P_2O_5 \cdot 12\ VO_2 \cdot 6\ V_2O_5 \cdot 5\ (NH_4)_2O + 7\ aq.$$

9 : 9 : 8 *Ammonium-salt.* — When boiling water is poured upon the black salt, it instantly becomes deep olive-green upon the surface, and then dissolves to a deep green liquid, which on cooling deposits crystals with a dull olive-green surface color. These may be redissolved and recrystallized a second time. The mother liquor from these crystals has a bright green color, and contains much vanadic acid. In the olive-green salt,

0.4061 gr. gave 0.0167 gr. $(NH_4)_2O$ = 4.12%
{ 0.2871 gr. " 0.1370 gr. As_2S_3 = 44.61%
{ 0.2871 gr. " 0.1393 gr. V_2O_5 by $KMnO_4$ = 48.51% (complete oxidation)
0.1637 gr. gave 0.0259 gr. VO_2 by $KMnO_4$ = 15.82%

The analyses correspond tolerably well with the formula

$$9\ As_2O_5 \cdot 9\ VO_2 \cdot 8\ V_2O_5 \cdot 4\ (NH_4)_2O + 11\ aq,$$

which requires:

		Calc'd.		Found.	
9 As_2O_5	2070	44.17	60.17	44.61	60.43
9 VO_2	750	16.00		15.82	
8 V_2O_5	1461	31.17		31.17	
4 $(NH_4)_2O$	208	4.44		4.12	
11 H_2O	198	4.22		4.28 (diff.)	
	4687	100.00			

The formula given must be doubled to give a structural scheme in which all the terms will be symmetrically arranged.

It appears at least probable that classes of antimonio-vanadates and antimonio-vanadico-vanadates also exist, but the few experiments which I have been able to make with the small quantity of material at my disposal are not conclusive as to either point, and I hope to be able to return to the subject.

VANADICO-VANADATES.

Salts belonging to this series are formed when solutions of vanadates are mixed with those of vanadic dioxide, and when vanadates undergo partial reduction by the action of any reducing agent. These compounds are often crystalline and well defined. They have, usually at least, a green color.

2 : 4 *Ammonic Vanadico-vanadate.* — When a solution of vanadic dioxide in chlorhydric acid is added to one of ammonic metavanadate, a fine green crystalline salt separates, but slightly soluble in either cold or hot water. The salt analyzed was not recrystallized, but merely washed with cold water and dried upon woollen paper. Of this salt,

$$\left\{\begin{array}{l} 1.0470 \text{ gr. gave } 0.0159 \text{ gr. } VO_2 \text{ by } KMnO_4 = 15.21\% \; VO_2 \\ 1.0470 \text{ gr. `` } 0.0701 \text{ gr. } V_2O_5 \text{ `` } = 66.98\% \; V_2O_5 \end{array}\right.$$
$$0.1470 \text{ gr. `` } 0.0066 \text{ gr. } (NH_4)_2O = 4.50\%$$

The analyses lead to the formula

$$4\ V_2O_5 \,.\, 2\ VO_2 \,.\, (NH_4)_2O + 8\ aq,$$

which requires

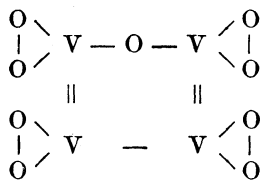
		Calc'd.	Found.
$4\ V_2O_5$	730.4	66.82	66.98
$2\ VO_2$	166.6	15.24	15.21
$(NH_4)_2O$	52	4.76	4.50
$8\ H_2O$	144	13.18	13.31 (diff.)
	1093	100.00	

The following may serve as starting-points for further investigation. When solutions of sodic divanadate and manganous sulphate are mixed and allowed to stand in an open vessel, very dark green well-defined crystals are gradually deposited. There is here, doubtless, reduction from the presence of dust. When a solution of vanadic dioxide in chlorhydric acid is mixed with solutions of the sulphates of zinc, copper,

cobalt, or nickel, and of sodic divanadate, dark green crystalline precipitates are formed on standing, which would appear to be vanadico-vanadates, but which, as they are formed in the presence of an excess of a strong acid, may prove to be types of vanadico-vanadic acids. In his valuable paper on the salts formed by vanadic acid, Rammelsberg has described a remarkable compound, which may be regarded as an anhydride of a special form of vanadico-vanadic acid. This compound has the formula

$$V_2O_5 + 2\,VO_2,$$

and forms black microscopic crystals. Its structural formula may be written:



It is easy to see how acids of various types might be derived from such anhydrides by replacing oxygen by an equivalent of hydroxyl. The existence of very well defined series of phosphoroso-tungstates and phosphoroso-molybdates, and of similar series of compounds containing As_2O_3 and Sb_2O_3, would naturally lead to the attempt to form similar classes of complex acids containing V_2O_3. Want of material has prevented me from experimenting in this direction, and I must content myself with directing the attention of other chemists to the subject. Vanadic protoxide appears to possess the properties of a base only, but our knowledge of the subject is so imperfect that it may also be well worth while to determine whether there may not be a class of vanadium compounds corresponding to the hypophospho-tungstates and hypophospho-molybdates.

The existence of classes of phospho-vanadates and arsenio-vanadates embraced under the general formula

$$R_2O_5 \,.\, V_2O_5 \,.\, n\, H_2O$$

would seem to imply that of corresponding chlorides, bromides, etc., of corresponding or analogous types,

$$R'Cl_5 \,.\, RCl_5\,, \quad R'Cl_4 \,.\, RCl_5\,, \text{ etc.}$$

Various compounds of this kind have already been observed by chemists, though, so far as I am aware, no attempt has been made to classify

them or to assign to them their true position as double chlorides, etc., corresponding to double oxides capable of forming complex acids. Examples of this class are the following: —

$SnCl_4$	+	PCl_5	Casselmann.
$SnCl_4$	+	$POCl_3$	"
$TiCl_4$	+	$POCl_3$	Weber.
$TiCl_4$	+	PCl_5	Tüttschew.
$SeCl_4$	+	$SbCl_5$	Weber.
$VOCl_2$	+	$PtCl_4$	Brauner.
Al_2Cl_6	+	$2\ POCl_3$	Casselmann.
Fe_2Cl_6	+	$2\ POCl_3$	"
$SbCl_5$	+	PCl_5	Weber.
$SbCl_5$	+	$POCl_3$	"

It is at least possible that in these and many similar cases complex or double acids correspond to the double chlorides, and it is probable that the action of such double chlorides upon solutions of acid tungstates and molybdates would produce complex acids containing tungsten or molybdenum and the two acid-forming oxides corresponding to the two united chlorides. I shall at another time specially consider the compounds of platinous and phosphorous chlorides discovered by Schützenberger.

In my paper upon the vanadium compounds of tungsten and molybdenum I have endeavored to show that many formulas may be reduced to the same types as those of the phospho-tungstates and phospho-molybdates, provided that we assume that a part at least of the vanadic pentoxide is to be regarded as replacing tungstic or molybdic oxide, or that we have the chemical equivalence expressed by the equation

$$m\ V_2O_2\ .\ O_3 = m\ WO_3 = m\ MoO_3.$$

This hypothesis had the advantage of simplifying many formulas materially, but was wholly unsupported by any positive evidence. I have now shown that there exist classes of phospho-vanadates and arsenio-vanadates which do not contain tungstic or molybdic oxide, but which are exactly parallel to phospho-tungstates, vanadio-tungstates, etc. in composition. Thus we have the salt,

$$12\ V_2O_5\ .\ P_2O_5\ .\ 3\ BaO + 45\ aq\ ;$$

and the acid,

$$20\ V_2O_5\ .\ P_2O_5\ .\ 6\ H_2O + 53\ aq\ ;$$

corresponding to

$$12\ WO_3 \,.\, P_2O_5 \,.\, 3\ BaO, \quad \text{and} \quad 20\ WO_3 \,.\, P_2O_5 \,.\, 6\ H_2O.$$

As regards the mode of replacement, however, our views must depend upon the special form of structural formulas which we provisionally adopt. With the view which I have taken of the subject, we may write for a phospho-vanadic acid assumed to have the formula

$$6\ V_2O_5 \,.\, P_2O_5 \,.\, 3\ H_2O,$$

corresponding to the phospho-tungstic acid

$$6\ WO_3 \,.\, P_2O_5 \,.\, 3\ H_2O,$$

the structural formula,

$$\begin{array}{rcccccl} & \overline{\text{Vl}O_2} & - & O - O & - & \overline{\text{Vl}O_2} & \\ & | & & & & | & \\ & \text{Vl}O_2 & - & O - O & - & \text{Vl}O_2 & \\ & \text{Vl}O_2 & - & O - O & - & \text{Vl}O_2 & \\ & | & & & & | & \\ 3\ (OH) \equiv & PO & & \text{———————} & & OP & \equiv (OH)\ 3, \end{array}$$

exactly like

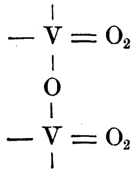
$$\begin{array}{rcccccl} & \overline{WO_2} & - & O - O & - & \overline{WO_2} & \\ & WO_2 & - & O - O & - & WO_2 & \\ & WO_2 & - & O - O & - & WO_2 & \\ & | & & & & | & \\ 3\ (OH \equiv & PO & & \text{———————} & & OP & \equiv (HO)\ 3. \end{array}$$

In the formula of the phospho-vanadic acid assumed, I have represented the complex V_2O_2 by Vl; and it is easy to see how, structurally, this may be regarded as hexatomic, and as replacing W^{VI} or Mo^{VI}, since we may reasonably suppose that we have

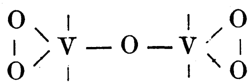
$$\begin{array}{ccc} O & - & V \equiv \\ | & & | \\ O & - & V \equiv . \end{array}$$

With this view of the subject $(V_2O_2)O_2 = WO_2 = MoO_2$, etc. This mode of formulating compounds containing vanadic pentoxide enables us, as I have shown, to reduce many complex salts to relatively simpler types, and is supported, as we shall presently see, by the formulas of a special class of vanadates exactly corresponding to meta-

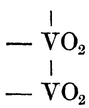
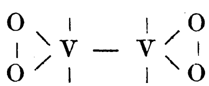
tungstates and metamolybdates. On the other hand, in by far the greater number of compounds thus far studied, the complex is to be regarded, I think, as built up of terms of the form RO_2, which may or may not be linked together by one or more atoms of oxygen. In certain cases, therefore, vanadic pentoxide may enter the complex with the structural formula



or as



This last view is strongly supported by the frequent presence of vanadic dioxide, two molecules of which may be considered as associated without a link of oxygen, as in the structural formulas

 and .

Finally, as I shall also prove, the structural formula must show what particular modification of phosphoric or vanadic oxide or acid is contained in the salt, since we have not merely ortho-phospho-tungstates but pyro-phospho-tungstates, various modifications of meta-phospho-tungstates, and corresponding compounds of molybdenum. It is at least probable that the different modifications of vanadic pentoxide or acid enter in a similar manner. These appear to be very numerous, and a wide field is thus opened for research. I shall return to this subject in the purely theoretical portion of my work.

If the view which I have taken as to the composition of the complex acids containing vanadium be correct, we ought to find some additional support for it in the constitution of the salts of vanadic acid. These have been studied by Roscoe, and especially by Norblad * and by Rammelsberg,† but the results obtained by these chem-

* Bidrag till kännedomen om Vanadiums Amfidsalter. Upsala Universitäts Årsskrift, 1873.

† Sitzungsberichte der Königl. Preuss. Akademie der Wissenschaften, 1883, p. 1.

ists have not been systematized. The very numerous vanadates may be arranged, as I find, under seven groups or series. These are here given for the sake of comparison, typical salts actually obtained in each series being marked by the initials of the analysts. The existence of salts corresponding to other general formulæ is a matter of inference only. As will be seen at once, the first series corresponds to the group of metatungstates, if we compare $V_2O_2 . O_3$ with WO_3. Terms 1 and 3 of this series of vanadates have twice the usually given molecular weights.

First Series.

	Vanadates.	Metatungstates.
	$R_2O . 4 V_2O_5$	$R_2O . 4 WO_3$
R.	$2 K_2O . 6 V_2O_5$	$2 R_2O . 6 WO_3$
N.	$3 Na_2O . 8 V_2O_5 + 24$ aq	$3 R_2O . 8 WO_3$
R.	$4 Na_2O . 10 V_2O_5 + 14$ aq	$4 R_2O . 10 WO_3$
	$5 R_2O . 12 V_2O_5$	$5 R_2O . 12 WO_3$

Second Series.

N.	$Na_2O . V_2O_5$
R.	$2 K_2O . 3 V_2O_5$
R.	$3 Li_2O . 5 V_2O_5$
	$4 R_2O . 7 V_2O_5$

Third Series.

R.	$K_2O . 2 V_2O_5 + 4$ aq
R.	$3 Li_2O . 4 V_2O_5 + 12$ aq
R.	$5 Li_2O . 6 V_2O_5 + 30$ aq
	$7 R_2O . 8 V_2O_5$

Fourth Series.

R.	$3 Li_2O . 2 V_2O_5 + 15$ aq
	$4 R_2O . 4 V_2O_5$
	$5 R_2O . 6 V_2O_5$
	$6 R_2O . 8 V_2O_5$

Fifth Series.

R.	$2 K_2O . V_2O_5 + 3$ aq
	$3 R_2O . 3 V_2O_5$
	$4 R_2O . 5 V_2O_5$
	$5 R_2O . 7 V_2O_5$

Sixth Series.

	$4 R_2O . 2 V_2O_5$
R.	$5 K_2O . 4 V_2O_5 + 7$ aq
	$6 R_2O . 6 V_2O_5$
	$7 R_2O . 8 V_2O_5$

Seventh Series.

Ro.	$3 Na_2O . V_2O_5 + 16$ aq
	$4 R_2O . 3 V_2O_5$
	$5 R_2O . 5 V_2O_5$
	$6 R_2O . 7 V_2O_5$

The seven series which I have given embrace, I believe, all known types of vanadates. Each series may be represented by a general formula expressing the relation between the number of molecules of acid and basic oxides. These general formulæ are:

$$
\begin{array}{rl}
\text{I.} & n\, R_2O\,.\,2\,n + 1\,.\,V_2O_5 \\
\text{III.} & n\, R_2O\,.\quad n + 1\,.\,V_2O_5 \\
\text{II.} & n\, R_2O\,.\,2\,n - 1\,.\,V_2O_5 \\
? & n\, R_2O\,.\,2\,n - 2\,.\,V_2O_5 \\
\text{V.} & n\, R_2O\,.\,2\,n - 3\,.\,V_2O_5 \\
\text{IV.} & n\, R_2O\,.\,2\,n - 4\,.\,V_2O_5 \\
\text{VII.} & n\, R_2O\,.\,2\,n - 5\,.\,V_2O_5 \\
\text{VI.} & n\, R_2O\,.\,2\,n - 6\,.\,V_2O_5
\end{array}
$$

The arrangement here given makes it probable that at least one series remains to be discovered. Fleitmann and Henneberg have described a phosphate having the formula $6\ Na_2O\ .\ 5\ P_2O_5$. Such a compound would belong to a class of phosphates represented by the general formula — wanting among the vanadates —

$$n\, R_2O\,.\,2\,n - 2\,.\,P_2O_5.$$

Roscoe long since established the correspondence of the vanadates and phosphates up to a certain limit. Further investigation is required to show how complete the correspondence is. From an examination of the terms in the seven series of vanadates given above, it will appear that various isomeric modifications are probable among vanadates, and that these correspond, in *form* at least, to the various metaphosphates, — mono, di, tri, tetra, and hexa-metaphosphates of Fleitmann and Henneberg. These chemists have also described a class of phosphates corresponding to the first term of the fourth series of vanadates given above. The sodium salt has the formula

$$3\ Na_2O\,.\,2\ P_2O_5 + 18\ \text{aq}.$$

In the imperfect state of our knowledge, all such coincidences are worthy of attention. Another conclusion may perhaps be safely drawn from the systematic arrangement of the vanadates which I have given. This is that meta, pyro, and ortho-vanadates, and the similar compounds of phosphorus, arsenic, antimony, etc., are not *isolated*, but are terms of more complete series. Thus the fifth series embraces the pyro-vanadates and their homologues, while the ortho-vanadates form the first term of the seventh series. In all the series given except the third, the common difference or homologizing term is $R_2O\ .\ 2\ V_2O_5$; in the third series, it is $2\ R_2O\ .\ 2\ V_2O_5$. In some cases only particular terms may exist to represent an entire series, because the special conditions necessary for the stability of other terms may be absent as regards degree. Taking now into account

the analogy which I have shown to exist between $V_2O_2 . O_3$ and WO_3 or MoO_3, we may perhaps extend the above conclusions to the cases of the tungstates, molybdates, chromates, etc. Thus we may regard $K_2O . 2 CrO_3$ as the initial term of a series corresponding to the third series of vanadates. If we double the usual formula of potassic terchromate, and write it $2 K_2O . 6 CrO_3$, we shall have the second term in a series corresponding to that of the metatungstates, the first term being the tetrachromate $K_2O . 4 CrO_3$.

As a further support to my view that the metatungstates form a homologous series, I shall here describe two new tungstates obtained since the first part of this work was published.

16 : 3 : 4 *Sodio-ammonic Tungstate.*—I obtained this salt accidentally in attempting to prepare a series of glycero-phospho-tungstates. The thick syrupy liquid obtained by heating pulverized glacial phosphoric acid with glycerine, and allowing the mixture to stand for some days, was neutralized with ammonia and poured into a hot solution of 12 : 5 sodic tungstate. A beautiful white salt, in shimmering talcose scales, separated as the solution cooled. After careful draining, the salt was recrystallized for analysis. The crystals had a fatty lustre, and were quite easily soluble in hot water. No phosphoric acid could be found in the salt by the most careful testing, and no organic matter. In this salt,

2.3796 gr. lost on ignition	0.2825 gr.		= 11.87 %
{ 2.1691 gr. " "	0.2568 gr.		= 11.84 %
{ 2.1691 gr. gave	1.8209 gr.	WO_3	= 83.94 %
2.0956 gr. "	0.0973 gr.	$(NH_4)_2O$	= 4.64 %

The analyses correspond to the formula

$$16 WO_3 . 3 Na_2O . 4 (NH_4)_2O + 18 aq,$$

which requires:

		Calc'd.	Found.
16 WO_3	3712	83.79	83.94
3 Na_2O	186	4.20	4.21 (diff.)
4 $(NH_4)_2O$	208	4.69	4.64
18 H_2O	324	7.32	7.21
	4430	100.00	

This salt is especially interesting because it supplies a new term to the series of metatungstates, — the highest as yet obtained.

12 : 1 : 4 *Sodio-ammonic Tungstate.* — This salt was obtained accidentally in an attempt to prepare a series of ethylo-phospho-tungstates. Syrupy phosphoric acid and absolute alcohol were mixed and heated for half an hour to about 80° C., and the mixture allowed to stand twenty-four hours. Ammonia was then added in small quantities at a time until in excess, the liquid being kept cool, the object being to form an ammonic ethylo-phosphate. The solution was then poured into one of 12 : 5 sodic tungstate. After a few minutes an abundant precipitation took place of small shimmering scales, which were drained on the filter-pump, washed with cold water, then dissolved in hot water and filtered. A very small quantity of a very insoluble salt in scales remained undissolved. The filtrate soon gave an abundance of small talcose scales with a fatty lustre.

Of this salt,

1.0293 gr. lost on ignition	0.1399 gr.		= 13.60 %
1.3019 gr. " "	0.1766 gr.		= 13.57 %
1.0001 gr. gave	0.0618 gr.	$(NH_4)_2O$	= 6.18 %
1.0293 gr. "	0.8689 gr.	WO_3	= 84.46 %

The analyses correspond to the formula

$$12\ WO_3 \, . \, Na_2O \, . \, 4\ (NH_4)_2O + 14\ aq,$$

which requires :

		Calc'd.	Found.
12 WO_3	2784	84.22	84.46
Na_2O	62	1.87	1.94 (diff.)
4 $(NH_4)_2O$	208	6.29	6.18
14 H_2O	252	7.62	7.42
	3306	100.00	

No trace of phosphoric acid could be detected in the salt, which is perhaps only interesting as furnishing additional evidence of the existence of a class of meta-tungstates in which the ratio of the tungstic oxide to the oxygen of the base is as 12 : 5. In this, as in the 16-atom salt above described, the presence of an excess of free ammonia explains the absence of phosphoric oxide in the compound formed.

My work on the compounds of vanadium is far less complete and thorough than I could have wished, on account of the relatively very high cost of the material. I indulge the hope that what I have done

will be found at least substantially correct, and that the whole subject will soon receive the attention of other chemists, who may have a more abundant supply of vanadium salts at their disposal.

ARSENOSO-TUNGSTATES.

The alkaline salts belonging to this series are easily prepared by boiling arsenous oxide with strong solutions of acid tungstates, as, for example, with 12 : 5 or 10 : 4 sodic salt. The arsenous oxide should be in excess to secure complete saturation. The filtered solution on standing usually deposits crystals of arsenous oxide in greater or less quantity. The salts of this series are either colorless or pale yellow. They are not very easily oxidized in acid solutions, but in presence of an excess of alkali they absorb oxygen from the air and are converted into arsenio-tungstates. Bromine and chlorine readily oxidize such solutions. The arsenoso-tungstates are, as a rule, more soluble than arsenio-tungstates. They are very stable and well defined, and may as a class be embraced under the general formula

$$m\,WO_3\,.\,n\,As_2O_3\,.\,p\,R_2O,$$

in which n is usually greater than unity.

Analytical Methods. — Hydric sulphide precipitates arsenous sulphide from these salts, and usually without sensible reduction of the tungstic teroxide. It is best to precipitate from a hot solution, and to pass the current of the gas for a long time to insure complete decomposition. The arsenous sulphide may then be collected and weighed upon a Gooch asbestos filter. The tungstic oxide may be determined in the filtrate by mercurous nitrate in the usual manner. The simplest and most satisfactory method of determining the arsenic is by titrition with iodine in a solution containing an excess of sodic or potassic bicarbonate. Finally, it is possible to determine the arsenic by oxidizing the solution with bromine after adding an excess of an alkaline carbonate, and then precipitating the arsenic in the form of ammonio-magnesic arsenate. The precipitate must be redissolved in dilute chlorhydric acid and precipitated a second time.

The alkaline arsenoso-tungstates are, as a rule, easily soluble; the crystalline salts are often soft and gummy, though well defined. They appear in some cases to be decomposed more or less completely by solution and evaporation, with separation of arsenous oxide and formation of new salts of different series. In certain cases the addition of a salt of one of the heavy metals determines the precipitation of crystals

of arsenous oxide in quantity. It is well known that alkaline hydrates also dissolve arsenous oxide in a proportion more than sufficient to form definite salts, and that the solutions deposit crystals of arsenous oxide on standing.

9 : 1 *Ammonic Arsenoso-tungstate.* — A boiling strong solution of 12 : 5 sodic tungstate dissolves arsenous oxide very readily, and in large quantity. The solution on evaporation gives a colorless or very pale yellow thick gummy mass, which on re-solution leaves octahedral crystals of arsenous oxide. The solution of the sodic salt gives with ammonic chloride, after standing some time, beautiful pale yellow almost colorless prisms. These may be redissolved and recrystallized without decomposition. Of this salt,

1.2699 gr. lost on ignition 0.2750 gr. = 21.65% H_2O, As_2O_3, and NH_3
1.3508 gr. gave by titrition with iodine 0.1034 gr. As_2O_3 = 7.65%
1.9457 gr. " 0.2713 gr. NH_4Cl = 6.78% $(NH_4)_2O$
0.9776 gr. " 0.7732 gr. WO_3 = 79.09% by $Hg_2(NO_3)_2$ and ignition.

The analyses lead to the formula

$$18\ WO_3 \,.\, 2\ As_2O_3 \,.\, 7\ (NH_4)_2O + 18\ aq,$$

which requires:

		Calc'd.	Found.
18 WO_3	4176	79.39	79.09
2 As_2O_3	396	7.53	7.65
7 $(NH_4)_2O$	364	6.92	6.78
18 H_2O	324	6.16	6.48
	5260	100.00	

The salt may of course be regarded as a double salt, but in this class of salts, as in the arsenio-tungstates and phospho-tungstates, I am disposed to think that in all cases we have an even number of molecules of tungstic oxide united with at least *two* molecules of arsenous oxide. Further investigations are of course required to settle this question. Meantime, from the analogy of the baric salt, we may write the formula provisionally as

$$9\ WO_3 \,.\, As_2O_3 \,.\, 4\ (NH_4)_2O + 9\ WO_3 \,.\, As_2O_3 \,.\, 3\ (NH_4)_2O + 18\ aq.$$

9 : 1 *Baric Arsenoso-tungstate.* — A solution of sodic arsenoso-tungstate obtained as above gives a white crystalline precipitate with baric chloride which is nearly insoluble in water, and which was there-

fore only washed upon the filter and dried on woollen paper for analysis. In this salt,

1.1037 gr. ignited with WO_4Na_2 lost 0.1290 gr. = 11.69% H_2O
1.9764 gr. titrated with iodine gave 6.15%, 6.38%, 6.18% As_2O_3, mean 6.23%
1.5652 gr. gave 0.4358 gr. SO_4Ba = 18.28% BaO.

In determining the arsenous oxide the salt was first dissolved in very dilute chlorhydric acid, an excess of sodic bicarbonate being added before titrition. The analyses correspond with the formula

$$9\ WO_3 \,.\, As_2O_3 \,.\, 4\ BaO + 21\ aq,$$

which requires:

		Calc'd.	Found.
9 WO_3	2088	63.74	63.80
As_2O_3	198	6.04	6.23
4 BaO	612	18.68	18.28
21 H_2O	378	11.54	11.69
	3276	100.00	

The formula may be

$$18\ WO_3 \,.\, 2\ As_2O_3 \,.\, 8\ BaO + 42\ aq.$$

I have stated above that arsenoso-tungstates pass readily into arsenio-tungstates by oxidation and assumption of two additional atoms of oxygen. It seemed therefore natural to suppose that other simple or complex molecules might also be added to the molecule of arsenous oxide entering into the complex acid. I shall hereafter give the results of a detailed examination of this subject.

16 : 8 *Sodic Arsenoso-tungstates.* — Arsenous oxide dissolves readily in 10 : 4 sodic tungstate on boiling. When an excess of arsenic is present, the filtrate, after evaporation to the consistency of a syrup, deposits on spontaneous evaporation large colorless prismatic crystals. These dissolve readily in water without decomposition and may be recrystallized until perfectly pure. After four recrystallizations,

0.9451 gr. gave with CO_3NaH and iodine 0.2178 gr. As_2O_3 = 23.05%
0.6128 gr. " " " 0.1416 gr. " = 23.10%
1.1327 gr. gave 0.3237 gr. As_2S_3 = 23.01% As_2O_3
0.9225 gr. " 0.5005 gr. WO_3 = 54.26%
1.0614 gr. " 0.5781 gr. " = 54.46%
0.8517 gr. " 0.1238 gr. H_2O = 14.54%

The analyses agree well with the formula

$$16\ WO_3 \,.\, 8\ As_2O_3 \,.\, 9\ Na_2O + 55\ aq,$$

which requires:

		Calc'd.	Found.		
16 WO_3	3712	54.23	54.28	54.46	
8 As_2O_3	1584	23.14	23.05	23.10	23.01
9 Na_2O	558	8.16		8.04 (diff.)	
55 H_2O	990	14.47		14.54	
	6844	100.00			

The salt gives off vapors of arsenous oxide even on gentle heating, and the determination of the water cannot be made by the use of sodic tungstate. After many trials, it was found best to mix the salt in a porcelain boat with plumbic oxide and carefully heat in a combustion tube, collecting the water in asbestos drenched with sulphuric acid. This process, suggested by my assistant, Mr. Herman Schmidt, gave good results in this case. A solution of the salt gives white flocky crystalline precipitates with baric, strontic, and calcic chlorides. Mercurous nitrate gives a pale yellow precipitate, which becomes darker on heating, and finally takes a dirty greenish-white color. Argentic nitrate gives a milk-white precipitate, which remains suspended for a long time. Manganous sulphate gives no precipitate, but the solution becomes yellow, and after standing some time yields beautiful bright yellow tabular crystals. Ammonic and potassic arsenates and orthophosphates give white crystalline precipitates, which appear to be respectively arsenoso-arsenio-tungstates and arsenoso-phospho-tungstates. The mother liquor of the 16 : 8 salt gives on evaporation a few crystals in a thick colorless syrup, which, after a few days, forms a pale yellowish hard gummy mass. This may prove to contain a second arsenoso-tungstate. The best method of preparing the beautiful 16 : 8 salt in quantity will probably be to mix 12 : 5 or 10 : 4 sodic tungstate and arsenous oxide in the precise ratio indicated by the formula of the salt, and, after adding water, to boil until the arsenous oxide is dissolved.

ARSENOSO-MOLYBDATES.

Arsenoso-molybdates are formed under the same conditions as arsenoso-tungstates, by boiling solutions of acid molybdates with an excess of arsenous oxide. In this case also there is always a sort of

supersaturation, and arsenous oxide separates from the solution on cooling. The general statements made concerning the arsenoso-tungstates apply to these salts also. The general formula is

$$m\ MoO_3 \cdot n\ As_2O_3 \cdot p\ R_2O,$$

in which n is usually greater than unity. The salts are often beautifully crystalline.

Analytical Methods. — Arsenous oxide may be determined in these salts by oxidizing the solutions in presence of an excess of an alkaline carbonate by means of bromine, and precipitating as ammonio-magnesic arsenate. The precipitation must be repeated a second time, but the final treatment with ammonic sulphide, which I have recommended for the separation of phosphoric and molybdic oxides, is of course inadmissible. By far the best method of determining the arsenic in these salts is titrition with iodine after addition of an excess of an alkaliue bicarbonate. It is not possible to determine the oxides of molybdenum and arsenic together by precipitation with mercurous nitrate, since no amount of care suffices to prevent the volatilization of arsenic in the subsequent ignition. For the same reason, it is also very difficult to determine the water of crystallization by the ignition loss, as fumes of arsenous oxide are given off at temperatures which are much below that at which sodic tungstate fuses. The degree of facility with which this takes place varies with the salt to be analyzed. As regards the determination of the water, I have found it best to heat gently in a porcelain crucible, supported over a small iron cup heated from below, but even in this case the results are never very satisfactory. Arsenous oxide cannot be separated from molybdic oxide by hydric sulphide, since molybdic sulphide is always precipitated at the same time, even when phosphoric acid has been added in excess. I have, however, found that fairly good determinations of molybdic oxide may be made in many cases by dissolving, boiling with a small excess of ammonia, adding a little ammonic chloride, and finally precipitating with baric chloride. The baric molybdate may then be ignited and weighed upon an asbestos filter. The results, if not very accurate, are at least sufficiently close to be of great service as verifications of formulas.

8 : 2 *Baric Arsenoso-molybdate.* — A boiling strong solution of 14 : 6 ammonic molybdate dissolves arsenous oxide in large quantity, and very readily. The solution has usually a yellowish-green color from slight reduction of the molybdic teroxide. After filtration and evaporation upon a water-bath, it deposits an abundance of octahedral crys-

tals of arsenous oxide. The filtrate from these does not yield crystals on standing, but after evaporation upon the water-bath solidifies to a greenish gummy mass, readily soluble in water, often however leaving a residue of arsenous oxide. The solution of this gummy salt gives a white crystalline precipitate with baric chloride. The filtrate from this, after evaporation and standing, yields an abundance of beautiful very pale greenish crystals, which may be redissolved and recrystallized without decomposition. In this salt,

1.1230 gr.	lost on heating	0.1126 gr.	= 10.03%	
1.0548 gr.	gave	0.3258 gr. SO_4Ba	= 20.28%	BaO
0.3919 gr.	"	0.0678 gr. As_2O_3	= 17.31%	
0.5774 gr.	"	0.0995 gr. "	= 17.23%	
0.9729 gr.	"	1.0383 gr. MoO_4Ba	= 51.74%	MoO_3

The analyses lead to the formula

$$8\ MoO_3 \cdot 2\ As_2O_3 \cdot 3\ BaO + 13\ aq,$$

which requires:

		Calc'd.		Found.		
8 MoO_3	1152	51.41	69.08	51.74		69.01
2 As_2O_3	396	17.67		17.31	17.23	
3 BaO	459	20.48		20.28		
13 H_2O	234	10.44		10.03		
	2241	100.00		99.32		

The arsenous oxide was determined in the first analysis by boiling with a solution of sodic dicarbonate, filtering, and titrating with iodine; in the second, by direct titrition without previous filtration. The baryta was separated by fusion with sodic carbonate, and weighed as sulphate. The water was found by heating over a radiator until a constant weight was obtained, as it was impossible to ignite with sodic tungstate without volatilization of arsenous oxide.

The salt requires a very large quantity of water for solution. The dry salt in fine powder boiled with argentic nitrate gives a beautiful yellow crystalline salt. Thallous nitrate yields, under the same circumstances, a very pale yellow, also crystalline salt. The mercurous salt is pale yellow, but not distinctly crystalline.

12 : 5 *Arsenoso-molybdate of Ammonium.* — When a solution of zincous sulphate is added to one of the gummy arsenoso-molybdate of ammonium, no precipitate is found at first, but after a time colorless

crystals are formed which do not contain zinc, and which may be recrystallized without apparent decomposition. The salt dissolves in a large quantity of water to a colorless solution. It is only partially decomposed by boiling with mercurous nitrate. In this compound,

0.7105 gr.	gave	0.0326 gr. $(NH_4)_2O$	= 4.58%
0.9785 gr.	"	0.0455 gr. "	= 4.65%
1.2612 gr.	"	1.3720 gr. MoO_4Ba	= 52.74% MoO_3
1.3081 gr.	"	0.3856 gr. As_2O_3	= 29.48%
0.6044 gr.	"	0.1787 gr. "	= 29.55%

The analyses correspond fairly well with the formula

$$12\ MoO_3 \ .\ 5\ As_2O_3\ .\ 3\ (NH_4)_2O + 24\ aq,$$

which requires:

		Calc'd.		Found.		
12 MoO_3	1728	52.28	82.21	52.74		82.24
5 As_2O_3	990	29.94		29.48	29.55	
3 $(NH_4)_2O$	156	4.71		4.58	4.65	
24 H_2O	432	13.07		13.15		
	3306	100.00				

The reactions of this salt were studied by acting with metallic solutions upon the finely pulverized substance, so as to avoid, if possible, the decomposing action of water. In this manner cold solutions of argentic and thallous nitrates give beautiful colorless granular crystals. Baric chloride gives a white colorless salt more flocky than the ammonium compound. Manganous sulphate does not react in the cold, but on boiling for some time a beautiful pale canary-yellow crystalline salt is formed. Cupric sulphate does not act when cold, but on boiling a clear solution results.

6 : 3 *Arsenoso-molybdate of Manganese.* — A portion of the dry gummy mass of arsenoso-molybdate of ammonium, which had stood for some time in the laboratory, was redissolved and filtered from a small quantity of arsenous oxide. The filtrate gave no precipitate with manganous sulphate, but, on boiling, the fine green solution became much lighter in color, then turbid, and finally deposited very beautiful bright orange-colored octahedral crystals insoluble in water. Of this salt,

0.5961 gr. gave 0.2052 gr. As_2O_3	= 34.41%
0.7341 gr. " 0.1216 gr. $P_2O_7Mn_2$	= 8.28% MnO
0.6362 gr. lost on heating over a radiator 0.0428 gr.	= 6.73%

The analyses correspond to the formula

$$6\ MoO_3 \cdot 3\ As_2O_3 \cdot 2\ MnO + 6\ aq,$$

which requires:

		Calc'd.	Found.
6 MoO_3	864	50.59	50.58
3 As_2O_3	594	34.78	34.41
2 MnO	142	8.31	8.28
6 H_2O	108	6.32	6.73
	1708	100.00	

The molybdic oxide was determined by difference only. By mixing a solution of the gummy arsenoso-molybdate of ammonium with solutions of zincous and cupric sulphates respectively, after standing, beautiful octahedral crystals were deposited, which in the case of the zinc salt were colorless, in that of copper, of a fine green. The corresponding nickel salt was also in beautiful green octahedral crystals. In the zinc salt,

0.2378 gr. gave 34.52% As_2O_3 by titrition with iodine.
0.3115 gr. " 34.47% " " "
0.2169 gr. " 34.56% " " "

The formula

$$6\ MoO_3 \cdot 3\ As_2O_3 \cdot 2\ ZnO + 6\ aq$$

requires 34.38%. In the copper salt,

0.2619 gr. gave 34.67% As_2O_3 by titrition with iodine.
0.2006 gr. " 34.89% " " "

The formula

$$6\ MoO_3 \cdot 3\ As_2O_3 \cdot 2\ CuO + 6\ aq$$

requires 34.41%.

In the cases of both the zinc and copper salts a trace of free arsenous oxide was probably mixed with the salt analyzed. The nickel salt doubtless corresponds to the other three. In the case of the manganese salt, fumes of arsenous oxide were given off at very low temperatures. The pale canary-yellow manganese salt obtained by precipitating the 12 : 5 ammonic salts with manganous sulphate corresponded to the formula

$$6\ MoO_3 \,.\, 3\ As_2O_3 \,.\, 2\ MnO + 15\ aq.$$

0.1727 gr. gave 31.77, 31.62, and 31.73% As_2O_3 by titrition with iodine.
1.1393 gr. " 0.0898 gr. Mn_3O_4 = 7.33% MnO.

The formula given requires 31.77% As_2O_3 and 7.59% MnO. The salt gave off arsenous oxide very freely when heated with sodic tungstate.

PHOSPHOROSO-TUNGSTATES.

I have already described the class of phosphoroso-molybdates, and will now consider the parallel group of phosphoroso-tungstates. The alkaline salts of this series are readily formed by the action of phosphorous and chlorhydric acids upon metatungstates of the higher order. They are, as a rule, better defined than the corresponding phosphoroso-molybdates, and are in all probability very numerous. The compounds to be described will be sufficient to open the subject for further investigation. The analytical methods employed were the same as in the case of the corresponding molybdenum salts, except that after oxidation of phosphorous to phosphoric acid, tungsten and phosphorus were usually precipitated together by mercurous nitrate and mercuric oxide.

22 : 4 : 6 *Ammonic Phosphoroso-tungstate.* — When the solution of phosphorous and chlorhydric acids formed by the action of water upon phosphoric terchloride is poured upon crystalline 12 : 5 ammonic tungstate, the salt packs at once into a dense mass. This is to be well rubbed up in a mortar with a large excess of the acid liquid, and allowed to stand for twenty-four hours. The greater part of the mass then presents large granular colorless crystals. A much smaller proportion of a white fine-grained salt is formed at the same time, and is easily separated by washing from the heavier crystals of the granular salt. This last may be washed with cold water on the filter pump, and dried on woollen paper. In mass the crystals present a faint but distinct tinge of yellow. The salt is but slightly soluble in cold water, but dissolves in a rather large proportion of boiling water to a yellow liquid. The solution gives no precipitate with cupric sulphate, but the mixed liquid becomes somewhat darker on boiling. With argentic nitrate it gives a turbid solution, which becomes purplish on heating, and finally gives a dark dull-purple precipitate. With mercurous nitrate the solution gives a white light precipitate, which becomes deep yellow on heating, and regains its white color on cooling. In this salt,

1.6407 gr. gave 0.1136 gr. $P_2O_7Mg_2$ = 5.12% PO_3H_3
1.7666 gr. " 0.1256 gr. " = 5.26% "
1.5933 gr. " 0.0791 gr. $(NH_4)_2O$ = 4.96%
1.7340 gr. lost with WO_4Na_2 0.2253 gr. = 12.99%

The analysis is of course subject to the corrections indicated by the equation

$$2\ PO_3H_3 = P_2O_5 + OH_2 + 4\ H.$$

The results agree very well with the formula

$$22\ WO_3 \,.\, 4\ PO_3H_3 \,.\, 6\ Am_2O + 25\ aq,$$

or

$$22\ WO_3 \,.\, 4\ \{H \,.\, PO \,.\, 2\ OH\}\ 6\ (NH_4)_2O + 25\ aq,$$

which requires:

		Calc'd.	Found.	
22 WO_3	5104	82.40	82.46	
4 PO_3H_3	328	5.29	5.26	5.12
6 $(NH_4)_2O$	312	5.04	4.96	
25 H_2O	450	7.27	7.32	
	6194	100.00		

The phosphorous acid was oxidized by bromine after adding an excess of sodic carbonate. The salt is quietly decomposed by heating, giving a mixture of $WO_3 \,.\, W_2O_5$ and P_2O_5.

32 : 16 : 5 *Potassic Phosphoroso-tungstate.* — This salt was formed, like the ammonium salt, by the action of a mixture of phosphorous and chlorhydric acids upon crystallized 10 : 4 potassic tungstate. In this case, also, two salts appear to be formed, — a heavier colorless crystalline salt in relatively large quantity, and a lighter fine-grained salt easily removed by careful washing. Of these, only the first was examined. Of this salt,

1.4225 gr. gave 1.2124 gr. oxides = 85.23% $WO_3 + P_2O_5$
1.3877 gr. " 0.2428 gr. $P_2O_7Mg_2$ = 11.19% P_2O_5 = 12.96% PO_3H_3
1.3949 gr. lost 0.1406 gr. = 10.08%

The analyses correspond to the formula

$$32\ WO_3 \,.\, 16\ PO_3H_3 \,.\, 5\ R_2O + 46\ aq,$$

or

$$32\ WO_3 \,.\, 16\ \{H \,.\, PO \,.\, 2\ OH\}\ 5\ R_2O + 46\ aq,$$

which requires:

		Calc'd.	Found.
32 WO_3	7424	73.97	74.04
16 PO_3H_3	1312	13.07	12.96
5 R_2O	472	4.70	4.69 (diff.)
46 H_2O	828	8.26	8.31
	10036	100.00	

The salt is but slightly soluble even in boiling water. It has no yellow tint.

22 : 8 : 2 *Sodic Phosphoroso-tungstate.* — This salt was formed, like the last, by the action of a mixture of phosphorous and chlorhydric acids upon crystallized 10 : 4 sodic tungstate. The action is very energetic. The colorless crystals of the tungstate soon disappear, and are replaced by yellow granular crystals in large quantity. The yellow crystals were well washed upon the filter-pump with cold water, and dried on woollen paper. Of this salt,

1.7082 gr. gave 1.4895 gr. oxides $= 87.19$ % $WO_3 + P_2O_5$
1.3623 gr. " 0.1870 gr. $P_2O_7Mg_2 = 8.78$ % $P_2O_5 = 10.15$ % PO_3H_3
1.3532 gr. lost with WO_4Na_2 0.1481 gr. $= 10.94$ %

The analyses correspond to the formula

$$22\ WO_3 \,.\, 8\ PO_3H_3 \,.\, 2\ Na_2O + 35\ aq,$$

which requires:

		Calc'd.	Found.
22 WO_3	5104	78.36	78.40
8 PO_3H_3	656	10.07	10.15
2 Na_2O	124	1.90	1.87 (diff.)
25 H_2O	630	9.67	9.58
	6514	100.00	

The sodium salt is nearly insoluble in cold water, and but slightly soluble in boiling water. The undissolved portion takes a much brighter yellow color. As in the cases of the potassium and ammonium salts, a small quantity of a second salt, in very small crystals and of a white color, is formed at the same time.

PHOSPHOROSO-MOLYBDATES (*again*).

As the phosphoroso-molybdate of ammonium, which I have described in another part of this paper, appeared to contain a trace of phosphoric acid, I repeated the preparation with a perfectly pure solution of phosphorous acid obtained by the action of water upon phosphorous chloride. The liquid contained, of course, free chlorhydric acid, and was poured into a cold strong solution of 14 : 6 ammonic molybdate. A sulphur-yellow precipitate was at once formed, consisting of very minute talcose scales. The salt was washed on the filter-pump very thoroughly with cold water, and dried on woollen paper. It is readily soluble in hot water to a yellow liquid. The solution on boiling reduces mercuric chloride to mercurous chloride. It gives an abundant white, flocky precipitate with argentic nitrate, which on long boiling becomes darker. Finally, silver is reduced. In this preparation,

0.7247 gr. lost with WO_4Na_2	0.1150 gr.		=	15.87 %
0.8323 gr. gave	0.0386 gr.	$(NH_4)_2O$	=	4.64 %
0.7426 gr. "	0.0776 gr.	$P_2O_7Mg_2$	=	6.68 % P_2O_5
0.9517 gr. "	0.0994 gr.	"	=	6.68 % "

The phosphorous acid was oxidized by bromine in presence of an excess of CO_3NaH. The analyses correspond most nearly to the formula

$$24\ MoO_3 \cdot 4\ PO_3H_3 \cdot 4\ (NH_4)_2\ O + 25\ aq,$$

which requires:

		Calc'd.		Found.	
24 MoO_3	3456	77.80	85.18	77.45	85.16
4 PO_3H_3	328	7.38		7.71	
4 $(NH_4)_2O$	208	4.68	14.82	4.64	14.84
25 H_2O	450	10.14		10.20	
	4442	100.00			

The analyses confirm the formula first obtained, though the new salt contains eight molecules more of water of crystallization.

ANTIMONOSO-TUNGSTATES.

When solutions of an acid tungstate of sodium are boiled with antimonious oxide, the latter very slowly dissolves, and it is difficult to obtain perfectly saturated solutions. It is best to employ antimonious

oxide which has been freshly precipitated from the corresponding chloride by sodic carbonate and washed by decantation with cold water. If the precipitated oxide is allowed to stand for some time, it becomes crystalline, and is then no longer available. The solution of antimonoso-tungstate obtained in this manner has a yellow color, and there is no sensible reduction of tungstic teroxide. Instead of this process, the following may be employed with advantage. Freshly precipitated antimonious oxychloride, SbOCl, after washing with cold water, dissolves very readily in boiling solutions of alkaline tungstates of the metatungstic series. The solutions obtained in this way are also yellow. The oxychloride, on standing for some days, also becomes highly crystalline, and then dissolves with great difficulty. The solutions of sodic salts obtained as above become on evaporation thick and syrupy, and finally yield yellow gummy masses. There is in these cases also a tendency to supersaturation, as with the arsenoso-tungstates, though by no means to the same extent, and crystals of antimonious oxide (hydrate?) are sometimes deposited. The concentrated solution of the sodic salt obtained as above gives yellow oils with strong solutions of potassic or ammonic salts, which are but slightly soluble in a large excess of the latter. After pouring off the supernatant liquid, the oils may be redissolved in a small quantity of water, and again precipitated by a large excess of a concentrated solution of a potassic salt. I prefer for this purpose the bromide. Two or three repetitions of this process yield a nearly pure potassic antimonoso-tungstate, which may be advantageously used in the preparation of other salts. The alkaline salts of this series are either oily liquids or gummy masses with a pale yellow color, and very easily soluble. The solutions absorb oxygen rather slowly from the air, and are not easily oxidized by bromine or chlorine unless in presence of an excess of alkali, as, for example, sodic bicarbonate. They then pass into antimonio-tungstates. The general formula of the antimonoso-tungstates is

$$m\,WO_3 \,.\, n\,Sb_2O_3 \,.\, p\,.\,R_2O.$$

Analytical Methods. — The quantitative separation of antimony from tungsten in these compounds may be effected by the following methods. Hydric sulphide passed through the solution previously acidulated with chlorhydric acid precipitates antimonious sulphide completely, without any sensible reduction or precipitation of tungsten. An aliquot portion of the sulphide may then be heated in an atmosphere of dry carbonic dioxide, in the usual manner. This method applies to the

greater number of cases. In its place we may often, but not always, employ the following, which usually gives good results in the cases of the alkaline salts. Potassic cyanide, as free as possible from carbonate and cyanate, is to be fused in a crucible of Berlin porcelain, and then allowed to cool. A weighed portion of the antimonoso-tungstate is then to be placed upon the fused mass, and the whole cautiously heated to low redness, and kept for a short time at this temperature. The antimony is completely reduced to metal, and after the solution of the alkaline salts in cold water, and washing at first with water and afterward with alcohol, may be weighed upon an asbestos filter. It will be seen that this process is the same as that devised many years ago by myself for the separation of tin from tungsten, worked out in my laboratory by Mr. F. H. Talbutt,* and known as Talbutt's method. The process unfortunately does not apply to cases in which insoluble compounds are formed together with the reduced metallic antimony. As a rule, when the process is successful, the antimony is finally in the form of large bright metallic globules, but in some cases it forms on reduction wholly or partially a black powder containing tungsten, and the method then fails. In these cases an accurate result may be obtained by mixing the salt or the potassic cyanide with a quantity of potassic or sodic carbonate sufficient to completely saturate both the tungstic and antimonic oxides present. This variation in the application of the method is due to my assistant, Mr. Herman Schmidt. In determining antimonious or antimonic oxides by this process, there is, of course, the disadvantage that a higher is always estimated from a lower molecular weight. The following analyses will serve to show the degree of accuracy which may be obtained under favorable circumstances, the method applying to antimonio-tungstates as well as to the antimonoso series. In an antimonio-tungstate of potassium not of definite constitution,

1.0924 gr.	gave	0.4407 gr.	metallic antimony	=	53.79 %	Sb_2O_5
1.0316 gr.	"	0.4155 gr.	" "	=	53.71 %	"

In another compound,

0.9059 gr.	gave	0.2251 gr.	metallic antimony	=	33.13 %	Sb_2O_5
1.0312 gr.	"	0.2558 gr.	" "	=	33.08 %	"

Antimonious oxide may also be determined in these compounds by titrition with iodine, after adding to the solution an alkaline tartrate

* Am. Journal of Science and Arts, l. 7.

and an excess of sodic bicarbonate. It will be found advantageous to standardize the solution of iodine by means of pure crystallized antimonio-potassic tartrate, — of course, after addition of an alkaline dicarbonate.

The determination of tungstic oxide may be effected by first separating the antimony as sulphide, and then precipitating the hot solution with baric chloride, after adding ammonia in small excess. The baric tungstate may be weighed upon an asbestos filter. It is better, however, to precipitate the tungstic oxide by means of mercurous nitrate; only, in case this method is to be applied, the antimony must be precipitated as sulphide after the addition of dilute sulphuric acid, and chlorhydric acid must not be employed.

11 : 3 *Baric Antimonoso-tungstate.* — A solution of sodic antimonoso-tungstate, obtained as above, gives with baric chloride a heavy pale yellow curdy or indistinctly crystalline precipitate. This salt melts under hot water to a thick yellow oily liquid, which dissolves very slowly, requiring a large quantity of water for solution. The solution has a yellow color and an acid reaction. It gives pale yellow flocky precipitates, with mercurous, argentic, and thallous nitrates. Of this salt,

1.0722 gr.	lost on ignition with WO_4Na_2 0.0858 gr.		=	8.00 %
1.3057 gr.	gave	0.3318 gr. Sb_2S_3	=	21.78 % Sb_2O_3
1.3668 gr.	"	0.3371 gr. "	=	21.17 % "
1.2543 gr.	"	0.1440 gr. SO_4Ba	=	7.54 % BaO
1.4895 gr.	"	0.1709 gr. "	=	7.53 % "
1.9450 gr.	"	1.6599 gr. oxides ($WO_3 + Sb_2O_4$)	=	85.34 %

The analyses lead to the formula

$$11\ WO_3 \,.\, 3\ Sb_2O_3 \,.\, 2\ BaO + 18\ aq,$$

which requires:

		Calc'd.		Found.		
11 WO_3	2552	63.07	84.42	62.79	62.99	(diff.) 84.37
3 Sb_2O_3	864	21.35		21.17	21.78	
2 BaO	306	7.57		7.54	7.53	
18 H_2O	324	8.00		8.00		
	4046	100.00				

The salt may be reduced to the type

$$6\ WO_3 \,.\, Sb_2O_3 \,.\, BaO + 9\ aq,$$

if we suppose Sb_2O_3 partially to replace WO_3; but in view of the very frequent recurrence of 22 molecules of tungstic oxide among complex inorganic acids, I am disposed to double the formula given above, and to write

$$22\ WO_3 . 6\ Sb_2O_3 . 4\ BaO + 36\ aq.$$

In the yellow oily salt obtained by precipitating sodic antimonoso-tungstate by means of potassic bromide, and carefully washing with a cold strong solution of the bromide, the ratio of the tungstic to the antimonious oxide was determined and found to be nearly 8 WO_3 to 2 Sb_2O_3, so that there is probably a series of antimonoso-tungstates with the general formula

$$8\ WO_3 . 2\ Sb_2O_3 . n\ R_2O.$$

The quantity of solution taken gave 0.1091 gr. $Sb_2S_3 = 0.0935$ gr. Sb_2O_3, and 0.3417 gr. $WO_3 = 71.51\ \%\ WO_3$ and 21.49 % Sb_2O_3.

ANTIMONOSO-MOLYBDATES.

The salts of this series are readily formed by boiling antimonious oxychloride, SbOCl, with an acid molybdate. The conditions are exactly the same as in the case of the corresponding antimonoso-tungstates. There is almost always a greater or less reduction of the molybdic oxide, and the solutions obtained have a greenish or greenish-blue tint from the presence of Mo_2O_5 or a similar oxide. The ordinary acid ammonic molybdate of commerce in cold solution readily dissolves freshly precipitated antimonious oxide with only a slight reduction of the molybdic oxide; on boiling, much reduction takes place.

Analytical Methods. — Antimonious oxide cannot be separated from molybdic oxide by means of hydric sulphide, as a greater or less proportion of molybdic sulphide is always found. By proceeding in the manner already pointed out for the separation of antimony from tungsten, it is possible, in many cases at least, to separate antimony from molybdenum with a very satisfactory degree of accuracy. It will be found, however, always advantageous to add a quantity of potassic or sodic carbonate sufficient to neutralize both the molybdic and antimonious oxides before fusion with potassic cyanide. Crucibles of the best Berlin porcelain are alone adapted to fusions of this kind, and even when these are employed the action of the alkaline mixture upon the crucible must be taken into account. The best method is to add

to the solution an alkaline tartrate, and then to render it alkaline with an excess of sodic bicarbonate. The antimonious oxide may then be determined by titrition with iodine.

17 : 3 *Ammonic Antimonoso-molybdate.* — This salt crystallizes from a solution of antimonious oxide in 14 : 6 ammonic molybdate, in pale greenish-yellow granular crystals, but its preparation is rather uncertain. It is insoluble in cold water: for analysis, the crystals were simply washed and dried upon woollen paper. In this salt,

0.7474 gr. gave by titrition with iodine 0.1618 gr. Sb_2O_3 = 21.65 %
0.5287 gr. " 0.0399 gr. $(NH_4)_2O$ = 7.55 %
1.0869 gr. lost on ignition with MoO_4Na_2 and WO_4Na_2 0.1851 gr. = 17.03 %.

The analyses lead to the formula

$$17\ MoO_3 \cdot 3\ Sb_2O_3 \cdot 6\ (NH_4)_2O + 21\ aq,$$

which requires:

		Calc'd.	Found.
17 MoO_3	2448	61.18	61.32
3 Sb_2O_3	864	21.59	21.65
6 $(NH_4)_2O$	312	7.79	7.55
21 H_2O	378	9.44	9.48
	4002	100.00	

The molybdic oxide is estimated by difference. The solution from which this salt of ammonium separated gave, after twenty-four hours, a fine yellow crystalline precipitate with manganous sulphate. The formula given may be reduced to the type

$$18\ MoO_3 \cdot 2\ Sb_2O_3 \cdot 6\ (NH_4)_2O + 21\ aq,$$

if we assume that one molecule of Sb_2O_3 plays the part of, or replaces, one molecule of molybdic oxide. In determining the water in this salt I employed a mixture of equal molecules of sodic tungstate and molybdate, which fuses at a temperature below that at which molybdic oxide is given off.

In formulating the arsenoso-tungstates and arsenoso-molybdates I have assumed provisionally that normal arsenites are represented by one or another of the three general formulas

$$As_2O_3 \cdot R_2O, \qquad As_2O_3 \cdot 2\ R_2O, \qquad As_2O_3 \cdot 3\ R_2O,$$

the three plumbic arsenites forming appropriate special instances. This view would establish a broad line of distinction between arsenites

and phosphites, which last are now generally considered as hydryl-phosphinates, the general formula being

$$H \,.\, PO \,.\, (OH)_2 \,.$$

On the other hand, the existence of alkyl-arsinic acids appears to prove beyond a doubt that at least *some* arsenites belong to the same type with the phosphites. The older view must in any case be true for certain classes of salts, because the arsenites are not all reducible to the type $H \,.\, AsO \,.\, (OH)_2$, even if we admit that the atom of hydrogen is replaceable by an atom of univalent metal, for which there is no sufficient evidence in the case of the phosphites. If we consider the arsenic in the arsenoso-tungstates and arsenoso-molybdates which I have described to exist in the form of hydryl-arsinic acid, we shall have for the corresponding acids, respectively, the formulas

$$\begin{array}{rl}
18\ WO_3 \,. & 4\ \{H \,.\, AsO \,.\, (OH)_2\} \,.\, 8\ H_2O \\
16\ WO_3 \,. & 16\ \{H \,.\, AsO \,.\, (OH)_2\} \,.\, 9\ H_2O \\
8\ MoO_3 \,. & 4\ \{H \,.\, AsO \,.\, (OH)_2\} \,.\, 3\ H_2O \\
12\ MoO_3 \,. & 10\ \{H \,.\, AsO \,.\, (OH)_2\} \,.\, 3\ H_2O \\
6\ MoO_3 \,. & 6\ \{H \,.\, AsO \,.\, (OH)_2\} \,.\, 3\ H_2O
\end{array}$$

in which, of course, the basicity is purely arbitrary, since it depends in each case upon the number of molecules of base in a single salt. The internal basicity, as measured by the hydroxyl in the arsenical term, is always two, corresponding to one in the old style of writing. As the salts described appear to give off all their water when heated without other decomposition than loss from the volatilization of arsenous oxide, it would seem to follow that their formulas must then at least be written as if they contained all the arsenic as As_2O_3, since

$$2\ \{H \,.\, AsO \,.\, (OH)_2\} = As_2O_3 + 3\ H_2O.$$

PHOSPHOROSO-PHOSPHO-TUNGSTATES.

24 : 1 : 2 : 5 *Potassic Phosphoroso-phospho-tungstate.* — When a solution containing both phosphorous and orthophosphoric acids is added to one of 12 : 5 sodic tungstate, no precipitate is formed, but on adding potassic bromide a white crystalline salt is thrown down, slightly soluble in cold water, but soluble in a large quantity of boiling water, forming a turbid liquid which has an acid reaction. The solution gives no precipitate with cupric sulphate, even on boiling and with or without free chlorhydric acid. It gives a white flocky precipitate with

argentic nitrate, which becomes darker on boiling, and finally deep chocolate-brown. This reaction resembles that of the phospho-hypo-phospho-tungstates. The solution gives a very pale yellow indistinctly crystalline precipitate with mercurous nitrate, which is not reduced by boiling, and a white flocky precipitate with baric chloride. The salt dissolves with much difficulty in ammonia-water, but easily in solutions of alkaline carbonates. Chlorhydric acid gives a white precipitate in these solutions, readily soluble in ammonia. In this salt,

$$\left\{\begin{array}{l}1.5373 \text{ gr. lost on ignition } 0.0578 \text{ gr.} = 3.76\% \\ 1.5373 \text{ gr. gave } 1.3702 \text{ gr. mixed oxides} = 89.13\%\ WO_3 \text{ and } P_2O_5\end{array}\right.$$

$$1.7603 \text{ gr. `` } 0.1138 \text{ gr. } P_2O_7Mg_2 = 4.13\%\ P_2O_5$$

$$2.7325 \text{ gr. `` } 0.0836 \text{ gr. `` } = 1.96\% \text{ ``}$$

In determining PO_3H_3 the solution in CO_3Na_2 was oxidized by bromine.

The analyses correspond with the formula

$$24\ WO_3 \cdot 2\ PO_3H_3 \cdot P_2O_5 \cdot 5\ K_2O + 13\ aq,$$

which requires:

		Calc'd.		Found.	
24 WO_3	5568	84.75	86.91	85.00	86.96
P_2O_5	142	2.16		1.96	
2 PO_3H_3	164	2.49		2.50	
5 K_2O	472	7.18		7.11	
13 H_2O	224	3.41		3.43	
	6570	100.00			

When a solution of phosphorous and chlorhydric acids is mixed with one of the 24 : 1 phospho-tungstate of sodium,

$$24\ WO_3 \cdot P_2O_5 \cdot 2\ Na_2O + 27\ aq,$$

no precipitate is formed, but after a time relatively large colorless measurable crystals of the phospho-tungstate are deposited.

PHOSPHOROSO-PHOSPHO-MOLYBDATES.

72 : 3 : 2 : 9 *Ammonic Phosphoroso-phospho-molybdate.* — When the solution of phosphorous and chlorhydric acids obtained by treating phosphorous terchloride with cold water is mixed with a solution of 10 : 2 ammonic phospho-molybdate, a greenish-yellow crystalline pre-

cipitate is thrown down at once. The salt is very insoluble in water. It was washed upon the filter-pump and dried on woollen paper for analysis. In this salt,

1.0222 gr.	lost with WO_4Na_2	0.0975 gr.	= 9.54%
0.8936 gr.	gave	0.0354 gr. $(NH_4)_2O$	= 3.96%
1.1348 gr.	"	0.0646 gr. $P_2O_7Mg_2$	= 3.63%
1.2439 gr.	"	0.0696 gr. "	= 3.58%

The determination of phosphoric oxide was made after oxidation by bromine.

The analyses agree very well with the formula

$$72\ MoO_3 \cdot 2\ PO_3H_3 \cdot 3\ P_2O_5 \cdot 9\ (NH_4)_2O + 38\ aq,$$

which requires:

		Calc'd.	Found.	
72 MoO_3	10368	85.61	85.56	
3 P_2O_5	426	3.52	3.58	3.63
2 PO_3H_3	164	1.35	1.50	
9 $(NH_4)_2O$	468	3.87	3.96	
38 H_2O	684	5.65	5.58	
	12110	100.00		

The formation of this salt may be represented by the equation

$$3\ \{24\ MoO_3 \cdot P_2O_5 \cdot 3\ (NH_4)_2O\} + 2\ PO_3H_3 =$$
$$72\ MoO_3 \cdot 3\ P_2O_5 \cdot 2\ PO_3H_3 \cdot 9\ (NH_4)_2O.$$

PHOSPHO-HYPOPHOSPHO-TUNGSTATES.

26 : 4 : 2 *Potassic Phospho-hypophospho-tungstate.* — When the 24 : 1 phospho-tungstate of sodium is boiled with an excess of a solution of hypophosphorous acid and a solution of potassic bromide is added to the clear pale blue filtrate, a white crystalline precipitate is after a time thrown down. The salt dissolves readily in hot water to a clear solution. This gives a white flocky crystalline precipitate with baric chloride, a pale yellow precipitate with mercurous nitrate, and a white precipitate with argentic nitrate, which on boiling becomes first yellow, then brown, and finally takes a brownish color, and deposits a precipitate closely resembling ferric hydrate. Cuprous sulphate is without action on the solution. For analysis the freshly formed salt

was thrown upon a filter, washed on the filter-pump thoroughly with cold water, and finally dried for analysis upon woollen paper. Of this preparation,

1.2162 gr.	gave	0.9706 gr.	mixed oxides	= 79.81%	
1.9865 gr.	"	1.5903 gr.	"	= 80.05%	
1.0921 gr.	"	0.1408 gr.	$P_2O_7Mg_2$	= 8.25%	P_2O_5
1.5059 gr.	"	0.1552 gr.	"	= 6.59%	"
1.2162 gr.	"	0.6340 gr.	$PtCl_6K_2$	= 10.12%	K_2O
0.9633 gr.	"	0.5074 gr.	"	= 10.22%	"
1.2705 gr.	lost with WO_4Na_2	0.1138 gr.		= 8.96%	
0.8472 gr.	" "	" 0.0778 gr.		= 9.18%	

In the analyses the hypophosphorous acid was determined by oxidation with bromine, after adding an excess of sodic carbonate. The total phosphoric acid was then determined as ammonio-magnesic phosphate. In another portion of the salt the phosphoric acid proper was precipitated directly by magnesia-mixture in the usual manner. Corrections are of course made for the loss of hydrogen in ignition, according to the equation

$$2\ PO_2H_3 + H_2O = P_2O_5 + 8\ H,$$

and also for the retention of one atom of oxygen by the mixed oxides, as shown by the same equation.

The analyses correspond to the formula

$$26\ WO_3 \cdot 2\ PO_2H_3 \cdot 4\ P_2O_5 \cdot 9\ K_2O \cdot Na_2O + 43\ aq,$$

or,

$$26\ WO_3 \cdot 2\ \{H_2 \cdot PO \cdot OH\} \cdot 4\ P_2O_5 \cdot 9\ K_2O \cdot Na_2O + 43\ aq,$$

which requires:

		Calc'd.	Found.	
26 WO_3	6032	71.66	71.56	71.80
4 P_2O_5	568	6.74	6.59	
2 PO_2H_3	132	1.57	1.55	
9 K_2O	850	10.09	10.12	10.22
Na_2O	62	0.74	0.78 (diff.)	
43 H_2O	774	9.20	9.23	
	8418	100.00		

It cannot be doubted that similar compounds containing molybdenum in place of tungsten remain to be discovered. I did not, how-

ever, succeed in obtaining them by the action of hypophosphorous acid upon phospho-molybdates, and the precise conditions necessary are yet to be determined. It appears to be at least probable that classes of phosphoroso-hypophospho-tungstates and phosphoroso-hypophospho-molybdates will sooner or later be discovered.

ARSENOSO-PHOSPHO-TUNGSTATES.

The salts of this series are formed when solutions of orthophosphates and arsenoso-tungstates are mixed, and when arsenous oxide is boiled with a solution of an alkaline phospho-tungstate. The alkaline salts are sometimes crystalline and sometimes gummy. The series is probably a very extensive one.

Analytical Methods. — In these salts the arsenous oxide is best determined by titrition with iodine after adding an excess of an alkaline dicarbonate. After separating arsenous oxide as sulphide by sulphydric acid, the phosphoric oxide may be determined by magnesia-mixture. Phosphoric and tungstic oxides may be determined together by mercurous nitrate and mercuric oxide after separating arsenous oxide from the solution as arsenous sulphide, dilute sulphuric acid being employed in place of chlorhydric acid. Water is best determined by heating over a radiator.

32 : 14 : 3 : 10 *Potassic Arsenoso-phospho-tungstate.* — This salt was prepared by boiling potassic phospho-tungstate with an excess of finely pulverized arsenous oxide. The filtered solution had a pale greenish-yellow tint, and after standing twenty-four hours deposited a mass of very minute greenish-yellow crystals. These were filtered off, washed with cold water, and then drained by the filter-pump. The drained mass was greenish yellow, and packed into a gummy solid. The filtrate on evaporation gave a fresh quantity of the same salt, which is rather soluble in cold, and very easily soluble in hot water. Of this salt,

0.9333 gr.	lost by heating over a radiator 0.0398 gr.	= 4.27 %
0.9333 gr.	gave 0.6094 gr. $WO_3 + P_2O_5$	= 65.29 %
1.0505 gr.	" 0.2413 gr. As_2O_3 with iodine	= 22.97 %
0.8456 gr.	" 0.0472 gr. $P_2O_7Mg_2$	= 3.57 %

The analyses correspond fairly well with the formula

$$32\ WO_3 \,.\, 14\ As_2O_3 \,.\, 3\ P_2O_5 \,.\, 10\ K_2O + 28\ aq,$$

which requires:

		Calc'd.		Found.	
32 WO_3	7424	61.51	88.00	61.72	88.26
14 As_2O_3	2772	22.96		22.97	
3 P_2O_5	426	3.53		3.57	
10 K_2O	944	7.82		7.58	
28 H_2O	504	4.18		4.27	
	12070	100.00			

12 : 2 : 2 : 6 *Sodio-potassic Arsenoso-phospho-tungstate.* — When sodic phospho-tungstate,

$$24\ WO_3 \cdot P_2O_5 \cdot 2\ Na_2O + 27\ aq,$$

in solution, is boiled with arsenous oxide in excess, this last dissolves freely to a colorless or nearly colorless liquid. On adding ammonic chloride no precipitate is formed, but after acidulating with chlorhydric acid a white crystalline precipitate is thrown down. On standing, the supernatant liquid deposits very distinct pale yellow tabular crystals. When potassic bromide is added to the sodic solution, a yellow oil separates after a time, which dries to a pale yellow gummy transparent mass. Of this salt,

0.9284 gr. lost over a radiator 0.0595 gr. = 6.41%
0.9492 gr. gave 0.0822 gr. As_2O_3 with iodine = 8.65%
1.2191 gr. " 0.1061 gr. " " = 8.70%
0.8961 gr. " 0.0944 gr. $P_2O_7Mg_2$ = 6.74% P_2O_5
0.8916 gr. " 0.6458 gr. $P_2O_5 + WO_3$ = 72.43%
0.8916 gr. " 0.5064 gr. $PtCl_6K_2$ = 11.03% K_2O

The formula which best represents the analyses is

$$12\ WO_3 \cdot 2\ As_2O_3 \cdot 2\ P_2O_5 \cdot 5\ K_2O \cdot Na_2O + 15\ aq,$$

which requires:

		Calc'd.	Found.
12 WO_3	2784	65.24	65.69
2 As_2O_3	396	9.28	8.65 8.70
2 P_2O_5	284	6.65	6.74
5 K_2O	472	11.06	11.03
Na_2O	62	1.45	1.48
15 H_2O	270	6.32	6.41
	4268	100.00	

The arsenous oxide is too low, but the sum of the arsenous and tungstic oxides, as well as the percentages of the other constituents of the salts, agree well with the formula.

60 : 1 : 4 : 7 *Potassic Arsenoso-phospho-tungstate.* — When a solution of potassic phosphate is poured into one of sodic arsenoso-tungstate as prepared by boiling arsenous oxide with 12 : 5 sodic tungstate, no precipitate is formed; but on adding chlorhydric acid the liquid becomes yellow, and, after standing, deposits beautiful pale yellow crystals. For analysis these were washed with cold water and dried on woollen paper. The salt is soluble in hot water, but appears to be decomposed by solution. In this salt,

1.2498 gr. gave 0.0671 gr. $P_2O_7Mg_2$	=	3.43% P_2O_5
1.2587 gr. " 0.0151 gr. As_2O_3 by iodine	=	1.20%
1.0348 gr. " 0.9192 gr. $WO_3 + P_2O_5$	=	88.81%
1.3143 gr. lost over a radiator 0.0787 gr.	=	5.99% water.

The analyses correspond closely to the formula

$$60\ WO_3 \,.\, As_2O_3 \,.\, 4\ P_2O_5 \,.\, 7\ K_2O + 55\ aq,$$

which may also be written

$$60\ WO_3 \,.\, 2\ AsO_3H_3 \,.\, 4\ P_2O_5 \,.\, 7\ K_2O + 52\ aq.$$

The formula requires:

		Calc'd.	Found.
60 WO_3	13920	85.21	85.38
4 P_2O_5	568	3.48	3.43
As_2O_3	198	1.21	1.20
7 K_2O	661	4.04	4.00 (diff.)
55 H_2O	990	6.06	5.99
	16337	100.00	

It is of course very possible that this may be a double salt, but there are at present no data upon which we can base a rational distribution of the components.

ARSENOSO-ARSENIO-TUNGSTATES.

The salts which belong to this group are formed under the same conditions as the corresponding arsenoso-phospho-tungstates. They are in many cases highly crystalline and well defined, and appear to be very numerous.

Analytical Methods. — Arsenic acid may be directly determined in the soluble salts of this series by means of magnesia-mixture, but it is best to redissolve the precipitated ammonio-magnesic arsenate in chlorhydric acid, and precipitate a second time by ammonia. Arsenous oxide may be determined by titrition with iodine after adding an excess of an alkaline dicarbonate. As a check upon the determination of the two oxides of arsenic, it is well to oxidize a portion of the salt directly by means of nitric acid, and then determine the total arsenic oxide by means of magnesia-mixture. A further check may also be obtained by reducing the arsenic oxide by boiling with sulphurous acid, and then titrating the total arsenous oxide by means of iodine. In solutions from which the arsenic has been completely removed as As_2S_3, tungsten can be determined by means of mercurous nitrate, provided that no chlorhydric acid or chloride is present.

21 : 1 : 4 : 10 *Potassic Arsenoso-phospho-tungstate.* — When potassic bromide is added to a solution of arsenoso-tungstate of soda, and a solution of potassic arsenate, AsO_4K_2H, is then poured into the clear filtrate, a white crystalline precipitate is formed. This salt requires a very large quantity of hot water for solution. Baric chloride boiled with it gives a well-defined flocky-crystalline salt. Argentic nitrate gives a similar salt, but this has a faint tinge of fawn-color, perhaps due to the presence of a trace of potassic arsenate not completely removed by washing. Mercurous nitrate gives on boiling a clear yellow flocky-crystalline salt. In the potassic salt,

1.9985 gr.	gave	0.3468 gr. $As_2O_7Mg_2$	= 12.36% As_2O_5
2.0085 gr.	"	0.0527 gr. As_2O_3 by iodine	= 2.62% As_2O_3

After complete oxidation by nitric acid,

1.5004 gr.	gave	0.3162 gr. $As_2O_7Mg_2$	= 15.63% As_2O_5
1.9684 gr.	"	1.2935 gr. WO_3	= 65.72%
1.5825 gr.	"	1.0346 gr. "	= 65.37%
1.3890 gr.	"	0.9382 gr. $PtCl_6K_2$	= 13.09% K_2O
1.5765 gr.	lost over a radiator	0.0955 gr.	= 6.06%

The analyses lead to the formula

$$21\ WO_3 \,.\, As_2O_3 \,.\, 4\ As_2O_5 \,.\, 10\ K_2O + 26\ aq,$$

which requires :

		Calc'd.	Found.	
21 WO_3	4872	65.86	65.72	65.37
As_2O_3	198	2.68	2.62	
4 P_2O_5	920	12.43	12.36	
10 K_2O	940	12.70	13.09	
26 H_2O	468	6.33	6.06	6.39 (diff.)
	7398	100.00		

Of course, in this salt, as in the arsenoso-phospho-tungstates described, arsenic may be supposed to be in the form of $\{H.AsO.(OH)_2\}$ either wholly or partially.

Classes of antimonoso-arsenio-tungstates, antimonoso-antimonio-tungstates, and arsenoso-antimonio-tungstates, appear also to exist and to be formed by processes exactly analogous to those described in the cases of the compounds containing two oxides respectively of the forms R_2O_3 and R'_2O_5, united with tungstic oxide.

ANTIMONOSO-PHOSPHO-TUNGSTATES.

These salts are formed under the same conditions as the corresponding arsenoso-phospho-tungstates, and the methods of analysis to be employed are the same.

22 : 6 : 5 : 12 *Potassic Antimonoso-phospho-tungstate.* — When a solution of potassic phosphate is poured into a hot solution of sodic antimonoso-tungstate as obtained by dissolving SbOCl in 10 : 4 sodic tungstate, a very pale yellow highly crystalline salt is at once formed. This is nearly insoluble in both hot and cold water. The portion analyzed was filtered off, washed upon the filter-pump with cold water, drained, and dried upon woollen paper. The salt, like many others which I have described, could not be recrystallized, but I give the results of the analyses for what they may prove to be worth. They certainly, I think, establish the existence of the series. In this salt,

{ 0.7776 gr.	gave	0.6142 gr. oxides	= 78.99%	
{ 0.7776 gr.	"	0.4763 gr. $PtCl_6K_2$	= 11.90%	
1.0323 gr.	"	with iodine 0.1594 gr. Sb_2O_3	= 15.44%	
0.9716 gr.	"	" 0.1509 gr. "	= 15.53%	
1.2300 gr.	"	0.1805 gr. $P_2O_7Mg_2$	= 9.20%	P_2O_5
1.2430 gr.	"	0.1821 gr. "	= 9.37%	"

The analyses lead to the formula:

$$22\ WO_3 \,.\, 5\ Sb_2O_3 \,.\, 6\ P_2O_5 \,.\, 12\ K_2O + 48\ aq,$$

which requires:

		Calc'd.	Found.	
22 WO_3	5104	54.34	54.23	
6 P_2O_5	852	9.07	9.20	9.37
5 Sb_2O_3	1440	15.33	15.44	15.53
12 K_2O	1133	12.07	11.90	
48 H_2O	864	9.19	9.13 (diff.)	
	9393	100.00		

ANTIMONIO-TUNGSTATES.

As already stated, these compounds are formed by the direct oxidation of antimonoso-tungstates, one molecule of oxygen being absorbed. I shall hereafter show that, in place of oxygen, platinous chloride and other divalent compounds may serve as complex replacing molecules. Antimonio-tungstates are also formed when antimonic hydrate in excess is boiled with an acid tungstate, and when tungstic teroxide is digested or boiled with an alkaline antimonate. The salts of this series are, as a whole, not so well defined as the phospho-tungstates, vanadio-tungstates, and arsenio-tungstates, and are much more difficult to prepare in a state of purity.

Analytical Methods. — These are essentially the same as those which I have given in the case of the antimonoso-tungstates. Antimonic and tungstic oxides may be precipitated together by mercurous nitrate and mercuric oxide. In the ignited precipitate it must be assumed that the antimony is in the form of tetroxide, Sb_2O_4, and the proper correction applied, after a special determination of the antimony, as sulphide or as metal.

6 : 2 *Antimonio-tungstate of Potassium.* — This salt was prepared by boiling potassic di-antimonate for a long time with a solution of 12 : 5 acid potassic tungstate. After filtration from a small quantity of the antimonate in excess, the filtrate, on standing twenty-four hours, deposited colorless granular crystals, which were washed with cold water and dried upon woollen paper. The salt was not very soluble in water; the crystals were soft and packed together between the fingers. In this salt,

1.0881 gr. lost on ignition with WO_4Na_2 0.1076 gr.	=	9.89 %
1.3566 gr. " " " 0.1379 gr.	=	10.16 %
1.4636 gr. gave 1.1178 gr. $WO_3 + Sb_2O_4$	=	76.36 %
1.3425 gr. " with KCy 0.2529 gr. Sb	=	25.12 % Sb_2O_5
0.9095 gr. " " 0.1700 gr. Sb	=	24.92 % "
0.8710 gr. " 0.5011 gr. $PtCl_6K_2$	=	11.16 % K_2O

The analyses lead to the formula

$$12\ WO_3\ .\ 4\ Sb_2O_5\ .\ 6\ K_2O + 25\ aq,$$

which requires:

		Calc'd.	Found.	
12 WO_3	2784	54.81	55.04	
4 Sb_2O_5	1280	25.19	25.12	24.92
6 K_2O	566	11.14	11.16	
25 H_2O	450	8.86	8.91	8.64
	5080	100.00		

In calculating the results of the analysis for comparison, I have assumed that, in the ignition with the sodic tungstate to determine the water, antimonic oxide is reduced to the tetroxide Sb_2O_4; a correction must therefore be applied to the apparent loss. This amounts to one twentieth of the percentage of antimonic pentoxide, and is of course to be deducted from the total loss. Chemists usually admit the existence of three classes of antimonates, corresponding respectively to metaphosphates, pyrophosphates, and orthophosphates, and formulas to support this view have been somewhat arbitrarily assigned to known compounds. If we suppose that the antimonio-tungstate above described contains metantimonic oxide, we may write the formula as we shall write those of corresponding metaphospho-tungstates,

$$12\ WO_3\ .\ 8\ SbO_3K\ .\ 2\ K_2O + 25\ aq.$$

A solution of this salt gives white crystalline precipitates with baric chloride, argentic nitrate, and cupric sulphate, and a yellow flocky-crystalline precipitate with mercurous nitrate.

ANTIMONIO-MOLYBDATES.

Salts belonging to this group are formed when freshly prepared antimonic hydrate is boiled with an acid molybdate in solution, when antimonic pentachloride in solution in chlorhydric acid is poured into a solution of an alkaline molybdate in small quantities at a time,

and when molybdic oxide is digested with a solution of an alkaline antimonate.

Analytical Methods. — The separation of antimony from molybdenum cannot be effected by sulphydric acid, because molybdic sulphide is always precipitated in greater or less quantity, even when phosphoric acid is present in the solution. The only method which I have been able to devise consists in fusing the salt to be analyzed or the mixture of oxides with potassic cyanide, as in the case of the separation of antimony from tungsten. In this case also it is always advisable, and sometimes necessary, to add a sufficient quantity of an alkaline carbonate to form a mixture of neutral molybdate and antimonate, as suggested by Mr. Herman Schmidt. With proper care the two oxides may be precipitated together by mercurous nitrate and mercuric oxide, and ignited without sensible loss of molybdic oxide; but there is then always a certain amount of reduced metallic antimony present, and on the whole the method is not to be recommended.

7 : 3 : 5 *Ammonic Antimonio-molybdate.* — Antimonic hydrate dissolves readily on boiling with a strong solution of 14 : 6 ammonic molybdate. The hydrate should be in excess, and should be added in small portions at a time, until, after long boiling, a part remains undissolved. After standing twenty-four hours, beautiful colorless crystals are deposited in quantity. These have a nacreous lustre, and are readily soluble in hot water. In this salt,

1.0647 gr. lost on ignition with WO_4Na_2 0.2052 gr. = 19.55 %
1.2234 gr. gave 0.2418 gr. NH_4Cl = 9.60 % $(NH_4)_2O$
0.9576 gr. " with KCy 0.3321 gr. Sb = 46.24 % Sb_2O_5.

The analyses correspond with the formula

$$7\ MoO_3 \cdot 4\ Sb_2O_5 \cdot 5\ (NH_4)_2O + 12\ aq,$$

which requires:

		Calc'd.	Found.
7 MoO_3	1008	36.47	36.52
4 Sb_2O_5	1280	46.31	46.24
5 $(NH_4)_2O$	260	9.40	9.60
12 H_2O	216	7.82	7.64
	2764	100.00	

The formula may also be written

$$7\ MoO_3 \cdot 8\ SbO_3NH_4 \cdot (NH_4)_2O + 12\ aq.$$

The solution of this salt gives with manganous sulphate after a time a fine canary-yellow crystalline precipitate. The ammonium salt appears to be decomposed by evaporation to dryness, or perhaps by the act of solution. The dry residue, on addition of water, leaves a white insoluble crystalline substance.

The existence of classes of vanadio-phospho-tungstates and vanadio-phospho-molybdates has already been proved. These may be embraced under the general formulas

$$m\ V_2O_5 \cdot n\ P_2O_5 \cdot p\ WO_3, \qquad m'\ V_2O_5 \cdot n'\ P_2O_5 \cdot p'\ MoO_3.$$

I believe that I am fully justified, though from qualitative experiments only, in maintaining that the formula

$$m\ R_2O_5 \cdot n\ R'_2O_5 \cdot p\ R''_2O_3$$

is general, and that R_2O_5 and R'_2O_5 may represent any two pentoxides, at least of the series P_2O_5 . V_2O_5 . As_2O_5 and Sb_2O_5.

PYROPHOSPHO-TUNGSTATES.

The phospho-tungstates and phospho-molybdates which have hitherto been described must be regarded as containing phosphoric oxide in the modification in which it exists in the class of tribasic or ortho phosphates. This appears to be clearly shown, first, by the synthesis of these compounds from orthophosphoric acid and orthophosphates and the acid tungstates and molybdates; and, secondly, from the fact that in all cases, after the addition of an excess of ammonia, magnesia-mixture at once throws down the characteristic ammonio-magnesic orthophosphate. I shall now show that the other modifications of phosphoric oxide or acid enter as such into similar compounds, so that we have perfectly well defined groups of pyrophospho-tungstates, metaphospho-tungstates, etc., and corresponding compounds containing molybdenum; and that, in the compounds so formed, the various modifications of phosphoric oxide preserve as it were their individuality. I shall further render it at least probable that there are groups — of phospho-tungstates for instance — in which two different modifications of phosphoric oxide may exist, each preserving its own characteristic properties. I do not now assert that in each of the complex groups which I have described orthophosphoric acid may be replaced by some other modification. That remains for experimental investigation. It is at least clear that the field already opened for study is one of

practically unlimited extent, as even an elementary application of the algebraical theory of permutations and combinations will show.

Pyrophospho-tungstates are formed when tungstic hydrate or tungstic oxide which has not been ignited is boiled with an alkaline pyrophosphate. The oxide readily dissolves, usually forming a yellow liquid. It is best to employ sodic pyrophosphate, as this gives a much more soluble salt, but the pyrophosphate must be specially prepared in the laboratory, and the tungstic oxide should be in excess. Neutral salts of the heavy metals usually give precipitates in solutions of the alkaline pyrophospho-tungstates; these precipitates are not necessarily salts of the same group, but are very often at least either pyrophosphates of the metallic bases or double pyrophosphates of the metal and of sodium or potassium.

Analytical Methods. — These are the same as those which I have employed in the case of the orthophospho-tungstates, only in the determination of the phosphoric oxide it is necessary to evaporate the salt two or three times in succession to dryness with an excess of chlorhydric acid, so as to convert the phosphoric acid present completely into the ortho or tribasic form. In the absence of any standard of comparison, it is necessary to speak with much hesitation, but it has always appeared to me that in these salts — in other words, in the presence of tungstic oxide — the conversion of pyrophosphoric acid into orthophosphoric acid is more difficult, or at least takes place more slowly, than in the case of the ordinary pyrophosphates. Tungstic and phosphoric oxides may in these compounds also be precipitated together by mercurous nitrate and mercuric oxide.

22 : 3 : 6 *Ammonio-sodic Pyrophospho-tungstate.* — A boiling solution of sodic pyrophosphate readily dissolves tungstic oxide as prepared by the action of chlorhydric or nitric acid upon calcic tungstate, but not ignited. The filtrate has a dull yellow color, and gives with a strong solution of ammonic chloride an abundant white crystalline precipitate, which cannot be purified by recrystallization, but which may be well washed upon the filter-pump with cold water, in which it is soluble to a very small extent. Hot water in large excess dissolves it, but even cold ammonia water dissolves it with much difficulty. When boiled for a long time with a solution of mercurous nitrate, the salt gives at first a white and finally a yellow mercurous salt. Argentic nitrate in solution gives at first with the salt extremely minute talcose scales, but on boiling for some time the whole dissolves to a clear liquid. When the salt is boiled with a solution of baric chloride, a flocky-crystalline white baric salt is formed. Cupric sulphate on boil-

ing dissolves the pyrophospho-tungstate, but on cooling a pale green crystalline body separates, which does not contain tungsten. The salt, precipitated by ammonic chloride as above, after washing with cold water and drying upon woollen paper, was analyzed:

0.6626 gr. lost on ignition 0.1060 gr. = 16.00 NH_3 and H_2O
0.9866 gr. gave 0.2479 gr. $P_2O_7Mg_2$ = 16.07 % P_2O_5
0.5488 gr. " 0.0499 gr. $(NH_4)_2O$ = 9.09 %
0.8188 gr. " 0.6504 gr. oxides = 79.46 % WO_3 and P_2O_5.

In determining the phosphoric oxide, the salt was several times in succession evaporated to dryness with nitric acid.

The analyses agree with the formula

$$22\ WO_3 \cdot 3\ \{P_2O_7Na_4\}\ 6\ \{P_2O_7(NH_4)_4\}\ 2\ (NH_4)_2O + 31\ aq,$$

which requires:

		Calc'd.	Found.
22 WO_3	5104	63.48	63.39
9 P_2O_5	1278	15.90	16.07
6 Na_2O	372	4.63	4.54 (diff.)
14 $(NH_4)_2O$	728	9.06	9.09
31 H_2O	558	6.93	6.91
	8040	100.00	

As already stated, the salt is dissolved by a large excess of hot water to a clear colorless solution. Cupric sulphate gives in this solution a pale blue crystalline precipitate of a pyrophosphate free from tungstic oxide. Argentic nitrate and baric chloride give white flocky-crystalline precipitates. Either, therefore, the salt is decomposed by solution or by the action of cupric sulphate.

22 : 9 : 18 *Potassic Pyrophospho-tungstate.* — When potassic bromide and acetic acid are added to the saturated solution of tungstic oxide in sodic pyrophosphate, a white granular fine-grained crystalline precipitate very slightly soluble in cold water is formed at once. For analysis the salt was washed upon the filter-pump with cold water, and dried on woollen paper. In this salt,

0.9440 gr. gave 0.6717 gr. oxides = 71.15% WO_3 and P_2O_5
1.3647 gr. " 0.9721 gr. " = 71.23% " "
0.9070 gr. " 0.2015 gr. $P_2O_7Mg_2$ = 14.21% P_2O_5
0.9817 gr. lost 0.0960 gr. H_2O = 9.78%

The phosphoric oxide was determined as before by evaporation with nitric acid to convert the pyrophosphoric into orthophosphoric acid.

The analyses correspond to the formula

$$22\ WO_3 \,.\, 9\ P_2O_7K_4 + 49\ aq,$$

which requires:

		Calc'd.	Found.	
22 WO_3	5104	56.94	56.94	57.02
9 P_2O_5	1278	14.26	14.21	
18 K_2O	1699	18.96	19.07	
49 H_2O	882	9.84	9.78	
	8963	100.00		

22 : 9 : 13 *Potassic Pyrophospho-tungstate.* — This salt was obtained by boiling tungstic oxide for some time with potassic pyrophosphate. After filtration and standing a white crystalline salt separated, which was well drained on the filter-pump, and then washed with cold water in which it is but slightly soluble. In much boiling water it dissolves on boiling to a clear liquid. The solution gives a white crystalline precipitate with argentic nitrate, — no precipitate at first with cupric sulphate. On boiling, a very pale blue crystalline salt separates, which does not contain tungsten, and is either a cupric pyrophosphate or a double salt of potassium and copper. The solution of the pyrophospho-tungstate gives a dense white distinctly crystalline precipitate with mercurous nitrate, and a turbid solution with baric chloride yielding on boiling a white feathery crystalline salt. No precipitate is formed with manganous sulphate, but after a short time the solution becomes turbid. In this salt,

1.6112 gr. gave 1.2119 gr. oxides	= 75.22%
1.9796 gr. " 1.4894 gr. "	= 75.23%
1.6421 gr. " 0.3862 gr. $P_2O_7Mg_2$	= 15.06%
1.2433 gr. lost by direct ignition 0.1299 gr.	= 10.45%

The analyses agree closely with the formula

$$22\ WO_3 \,.\, 6\ P_2O_7K_4 \,.\, 3\ P_2O_7H_4 \,.\, K_2O \,.\, H_2O + 42\ aq,$$

so that the type is, as in other cases,

$$22\ WO_3 \,.\, 9\ P_2O_7H_4 \,.\, 2\ R_2O.$$

The formula requires:

		Calc'd.	Found.	
22 WO_3	5104	60.11	60.17	60.18
9 P_2O_5	1278	15.05	15.05	
13 K_2O	1227	14.45	14.32 (diff.)	
49 H_2O	882	10.39	10.45	
	8491	100.00		

All the compounds of this group which I have obtained belong, as will be seen, to the same type which contains the frequently recurring chemical mass of twenty-two molecules of tungstic oxide, united to nine molecules of pyrophosphoric acid or a pyrophosphate, together with a certain amount of base over and above that required to saturate the phosphoric oxide. We may represent this group provisionally by a structural formula containing *nine* groups of the form:

$$\begin{matrix} HO \\ HO \end{matrix} \!\!>\! \overset{|}{\underset{|}{P}}O - O - O\overset{|}{\underset{|}{P}} \!<\!\! \begin{matrix} OH \\ OH \end{matrix}$$

Further investigation will doubtless show that there are other series of pyrophospho-tungstates and analogous pyrophospho-molybdates. It is especially desirable to study the compounds which remain in solution after the precipitation of part of the pyrophosphoric oxide by means of cupric sulphate.

It may here be remarked. that Wallroth * has described a series of pyrophosphates which contain *nine* molecules of P_2O_7, united in each case to thirty-six atoms of metal. Thus we have

$$Ca_{10}\ Na_{16}\ (P_2O_7)_9$$
$$Mg_{10}\ Na_{16}\ (P_2O_7)_9$$
$$Co_{10}\ Na_{16}\ (P_2O_7)_9$$
$$Ni_{10}\ Na_{16}\ (P_2O_7)_9 .$$

It would therefore appear that similar complex molecules enter directly into combination with twenty-two molecules of tungstic oxide, but that the complexity is not necessarily due to a determining action on the part of the latter.

* Bull. de la Soc. Chimique, [2,] xxxix. 316.

MONOMETAPHOSPHO-TUNGSTATES.

In preparing the salts of this series I have employed ordinary glacial phosphoric acid, which, according to Brescius,* contains about 50% of sodic metaphosphate, and which may be regarded as a mixture of sodic metaphosphate and metaphosphoric acid. I have assumed that the acid is here in the form of monometaphosphoric acid, although upon this point the evidence is still insufficient. As the relations of metaphosphoric acid to indicators of various kinds have not hitherto been studied, the following brief note may be of interest. A solution of glacial phosphoric acid is neutral to tropæolin. The same solution required for equal volumes with purpurin 23 cc. sodic hydrate solution; with hæmatoxylin, 14 cc.; and with alizarin, 12.5 cc. No definite end reaction could be obtained with phenol-phthalein, methyl-orange, or rosolic acid.

Monometaphospho-tungstates are formed by the direct action of the acid upon acid tungstates. They are, frequently at least, gummy uncrystalline bodies. When crystalline the crystals are usually soft, and pack together readily. The salts of the alkaline earths are usually more or less distinctly crystalline. Those of the heavy metallic oxides are often pasty, and sometimes oily. They are not very readily converted into orthophospho-tungstates, and in this respect they seem to differ materially from the corresponding metaphospho-molybdates.

Analytical Methods. — In these salts tungstic and metaphosphoric oxides may be precipitated together by mercurous nitrate and mercuric oxide. Metaphosphoric acid may be converted into orthophosphoric acid by dissolving the salt in the least possible quantity of water, adding strong sulphuric acid, evaporating the solution nearly to dryness, and repeating this process several times. This method is very much better than fusion with alkaline carbonates, which effects the transformation of metaphosphoric acid in a very imperfect manner. I believe that I can assert with entire confidence, that in the class of monometaphospho-tungstates the conversion of the metaphosphoric into orthophosphoric acid is much more difficult than in the metaphosphates. The precipitation of the orthophosphoric acid by magnesia-mixture must of course be repeated twice.

24 : 2 : 3 *Potassic Monometaphospho-tungstate.* — When a cold freshly prepared solution of glacial phosphoric acid is digested with 10 : 4 potassic tungstate, part of this salt dissolves, while the undissolved

* Zeitschrift für analytische Chemie, vi. 187.

portion changes its character, and is converted into a soft crystalline, very slightly soluble mass. This may be filtered off, and washed with cold water. In this salt,

$$\begin{cases} 1.5236 \text{ gr. lost on ignition } 0.0857 \text{ gr.} = 5.63\% \\ 1.5236 \text{ gr. gave } 0.0517 \text{ gr. } P_2O_7Mg_2 = 1.96\% \; P_2O_5 \end{cases}$$

$$0.9934 \text{ gr. `` } 0.0303 \text{ gr. ``} = 2.17\% \text{ ``}$$

$$1.0686 \text{ gr. `` } 0.0352 \text{ gr. ``} = 2.11\% \text{ ``}$$

$$\begin{cases} 1.1490 \text{ gr. `` } 1.0171 \text{ gr. oxides} = 88.52\% \\ 1.1490 \text{ gr. `` } 0.3327 \text{ gr. } PtCl_6K_2 = 5.70\% \; K_2O \end{cases}$$

The analyses correspond very well to the formula

$$24\, WO_3 \,.\, 2\,\{PO_3K\}\; 3\, K_2O + 20 \text{ aq},$$

which requires:

		Calc'd.	Found.
$24\, WO_3$	5568	86.36	86.38
P_2O_5	142	2.21	2.11 2.17 1.96
$4\, K_2O$	376	5.84	5.70 5.85 (diff.)
$20\, H_2O$	360	5.59	5.63
	6446	100.00	

The filtrate from the 24 : 2 salt, on standing, deposits a white crystalline salt, which, when thrown on a filter and washed with cold water, presents a colorless gummy mass. Of this salt,

$$0.6183 \text{ gr. gave } 0.0307 \text{ gr. } P_2O_7Mg_2 = 3.17\% \; P_2O_5$$

$$\begin{cases} 0.8173 \text{ gr. `` } 0.6844 \text{ gr. oxides} = 83.72\% \\ 0.8173 \text{ gr. lost on ignition } 0.0607 \text{ gr.} = 7.43\% \end{cases}$$

From an oversight, the potassic oxide was not determined in this salt, which may be either

$$16\, WO_3 \,.\, 2\,\{PO_3K\}\; 2\, K_2O \,.\, 2\, Na_2O + 20 \text{ aq},$$

or

$$16\, WO_3 \,.\, 2\,\{PO_3K\}\; 5\, Na_2O + 20 \text{ aq}.$$

The formulas require, respectively,

		Calc'd.		Found.	Calc'd.			
$16\, WO_3$	3712	80.34		80.56	80.38		3712	$16\, WO_3$
P_2O_5	142	3.07		3.17	3.07		142	P_2O_5
$3\, K_2O$	283	6.12	8.80	8.87	2.04	8.76	94	K_2O
$2\, Na_2O$	124	2.68			6.72		310	$5\, Na_2O$
$20\, H_2O$	360	7.79		7.40	7.79		360	$20\, H_2O$
	4621	100.00			100.00		4618	

18 : 1 : 2 *Ammonic Monometaphospho-tungstate.* — When 12 : 5 ammonic tungstate is boiled with a solution of glacial phosphoric acid, a white crystalline mass remains undissolved, very different in appearance from the ammonic tungstate employed. This salt requires a large quantity of boiling water for solution, but is only slightly soluble in cold water. For analysis, it was thoroughly drained upon the filter-pump, and then washed with cold water. Of this salt,

1.6896 gr. lost by ignition with WO_4Na_2 0.1082 gr.	$= 6.40\%$	
1.5026 gr. gave 0.0745 gr. $P_2O_7Mg_2$	$= 3.17\%$	P_2O_5
1.4267 gr. " 0.0316 gr. $(NH_4)_2O$	$= 2.21\%$	

The analyses correspond to the formula

$$18\ WO_3 \,.\, 2\ \{PO_3NH_4\} \,.\, (NH_4)_2O + 11\ aq,$$

which requires:

		Calc'd.	Found.
18 WO_3	4176	90.39	90.43
P_2O_5	142	3.08	3.17
2 $(NH_4)_2O$	104	2.25	2.21
11 H_2O	198	4.28	4.19
	4620	100.00	

The filtrate from this salt gives on evaporation a thick colorless syrup, in which white crystals — perhaps of the salt above described — were suspended. It will be seen that the action of PO_3H upon 12 : 5 ammonic tungstate is essentially the same as upon the 10 : 4 potassic salt, and that in each case at least one crystalline and one gummy salt are formed.

The analyses given are sufficient to establish the existence of three classes of monometaphospho-tungstates. My work on this subject is to be regarded merely as preliminary, and is intended to direct the attention of other chemists to this class of salts. In another paper I shall give the results of a more detailed study of the various metaphospho-tungstates. Fleitmann and Henneberg have described five series of metaphosphates; in addition to these, there remain to be studied, in their relation to tungstic and molybdic oxides, the two series of tetraphosphates, $P_4O_7 \,.\, 6\ RO$, and dekaphosphates, $P_{10}O_{19} \,.\, 12\ RO$, discovered by the same chemists, as well as the new group of salts described by Salzer,* which may be called hypophosphates.

* Pharmaceutische Zeitung, Bunzlau, 1881. Ann. der Chemie, ccxi. 1.

ORTHOMETAPHOSPHO-TUNGSTATES.

A single salt of this series will be sufficient to establish the existence of compounds into which two different modifications of phosphoric acid enter, to a certain extent at least preserving their peculiar characteristics.

22 : 6 : 11 : 7 *Potassio-sodic Orthometaphospho-tungstate.* — When 24 : 1 sodic phospho-tungstate is boiled with a solution of sodic monometaphosphate, PO_3Na, the salt dissolves readily to a clear liquid. Potassic bromide gives a white precipitate in this solution. After filtering and washing with cold water, a white gelatinous mass remains upon the filter, but slightly soluble in water. Of this salt,

1.2008 gr. gave 0.8728 gr. oxides	= 72.68%	
1.5959 gr. " 0.1611 gr. "	= 72.76%	
1.3558 gr. " 0.2220 gr. $P_2O_7Mg_2$	= 10.47%	P_2O_5
0.8822 gr. " 0.5774 gr. $PtCl_6K_2$	= 12.70%	K_2O
1.4517 gr. lost on ignition with WO_4Na_2 0.1349 gr.	= 9.29%	

The analyses correspond with the formula

$$22\ WO_3 \,.\, 6\ P_2O_5 \,.\, 11\ K_2O \,.\, 7\ Na_2O + 42\ aq,$$

which requires:

		Calc'd.	Found.
22 WO_3	5104	62.36	62.25
6 P_2O_5	852	10.41	10.47
11 K_2O	1038	12.68	12.70
7 Na_2O	434	5.31	5.29
42 H_2O	756	9.24	9.29
	8184	100.00	

The solution of this salt in chlorhydric acid gives, with magnesia-mixture and ammonia, a precipitate which appears to contain ammonio-magnesic phosphate and magnesic metaphosphate. It is of course possible that a portion of the metaphosphoric acid may have been converted into orthophosphoric acid by the act of solution in chlorhydric acid. I know of no method by which really reliable determinations, either qualitative or quantitative, can be made in compounds of this kind. In the analysis above, the salt was evaporated several times with strong sulphuric acid, and the phosphoric acid then determined with magnesia-mixture. The total quantity of base in the salt

is exactly sufficient to saturate six molecules of orthophosphoric acid, but the salt certainly contains at least a part of the phosphorus as metaphosphoric oxide. We may perhaps assume that the two modifications are equally divided between the bases, and the formula may then be written

$$22\ WO_3 \,.\, 3\,(P_2O_5 \,.\, 3\ K_2O) \,.\, 6\ PO_3Na \,.\, 2\ K_2O \,.\, 4\ Na_2O + 42\ aq.$$

The subject of course requires further investigation.

MONOMETAPHOSPHO-MOLYBDATES.

The salts belonging to this series appear also to belong to two different classes, which may be simply distinguished as crystalline and gummy salts. Both these classes are readily converted by acids into orthophospho-molybdates. Up to the present time I have made only a preliminary study of these compounds.

10 : 2 : 5 *Ammonic Monometaphospho-molybdate.* — When glacial phosphoric acid is neutralized with ammonia, and the solution is mixed with one of 14 : 6 ammonic molybdate, no precipitate is formed, but on evaporation a thick, nearly colorless gummy mass is formed. On standing for some time, this is almost completely converted into a crystalline mass. This may be drained, redissolved in water, in which it is very soluble, and recrystallized several times from very concentrated solutions. It then presents very beautiful, perfectly colorless, flat tabular crystals. The solution gives at once, with nitric acid, a precipitate of yellow orthophospho-molybdate; with magnesia-mixture and ammonia, a precipitate very different from ammonio-magnesic orthophosphate. Argentic nitrate gives a flocky-crystalline precipitate; baric and thallous nitrates give beautiful white feathery-crystalline salts; mercurous nitrate gives a pale flocky-crystalline precipitate, while cuprous sulphate forms none. Of this salt,

1.4314 gr. gave	0.3002 gr. $P_2O_7Mg_2$	= 13.41 %	P_2O_5
0.8385 gr. "	0.1022 gr. $(NH_4)_2O$	= 12.19 %	
1.4016 gr. lost	0.2776 gr.	= 19.81 %	

The analyses agree with the formula

$$10\ MoO_3 \,.\, 2\ P_2O_5 \,.\, 5\ (NH_4)_2O + 9\ aq,$$

which requires:

		Calc'd.		Found.	
10 Mo_2O_3	1440	67.10	80.33	66.78	80.19
2 P_2O_5	284	13.23		13.41	
5 $(NH_4)_2O$	260	12.12		12.19	
9 H_2O	162	7.55		7.62	
	2146	100.00			

The formula may be more advantageously written

$$10\ MoO_3 \,.\, 4\ \{PO_3NH_4\} \,.\, 3\ (NH_4)_2O + 9\ aq.$$

Empirically, this salt has, except as regards water of crystallization, the same formula as the acid 10 : 2 orthophospho-molybdate, which I have already described.

HEXAMETAPHOSPHO-MOLYBDATES.

The single salt of this series which I have thus far obtained will serve as an example, and I hope as an incentive to further study.

14 : 3 : 4 *Baric Hexametaphospho-molybdate.* — Sodic hexametaphosphate, obtained by heating the so-called microcosmic salt until a clear colorless glass is obtained, gives a white colorless crystalline salt with baric chloride, which, after washing with cold water, readily dissolves in an excess of a solution of 14 : 6 ammonic molybdate. After a short time the clear filtered solution deposits an abundance of beautiful colorless acicular crystals. This salt cannot be perfectly decomposed by boiling with a solution of mercurous nitrate. Nitric acid dissolves it to a turbid liquid, with formation of a yellow powder. After boiling with the acid, ammonic molybdate gives the characteristic yellow crystalline precipitate, indicating the presence of orthophosphoric acid. Of this salt,

1.0140 gr. lost on ignition with WO_4Na_2 0.2463 gr. = 24.31%
1.8970 gr. gave 0.4286 gr. SO_4Ba = 14.84% BaO
2.0403 gr. " 0.3454 gr. $P_2O_7Mg_2$ = 10.83% P_2O_5.

The formula appears to be

$$14\ MoO_3 \,.\, 3\ P_2O_5 \,.\, 4\ BaO + 55\ aq,$$

which requires:

		Calc'd.	Found.
14 MoO_3	2016	49.86	50.02
3 P_2O_5	426	10.53	10.83
4 BaO	612	15.13	14.84
55 H_2O	990	24.48	24.31
	4044	100.00	

I give this formula with much reserve, and only as probably correct. To express the presence of hexametaphosphoric oxide, it may be written

$$14\,MoO_3 \,.\, \{Ba_3 \,.\, 6\,PO_3\} \,.\, BaO + 55\,aq.$$

I shall return to the subject at another time.

STANNO-PHOSPHO-TUNGSTATES.

The vanadico-vanadio-tungstates and vanadico-vanadio-molybdates which I have described furnish instances of compounds embraced under the general formulas

$$m\,RO_3 \,.\, n\,R'O_2 \,.\, p\,R''_2O_5 \,.\, r\,R'''_2O.$$

I shall show that the compounds belonging to this type are very numerous, and frequently very well defined. For the present, it will be sufficient to cite two new series of hitherto undescribed salts, my object being to direct the attention of other chemists to a new field of investigation, and to point out methods of preparation and of analysis which may facilitate their work.

Stanno-phospho-tungstates are formed when the stanno-chlorides of ammonium or of the alkaline metals are mixed in solution with acid alkaline tungstates. They are colorless crystalline salts, so far as studied. As a representative of this series we may take the ammonium salt.

Analytical Methods. — In these salts the three higher oxides may be determined together by precipitation with mercurous nitrate and mercuric oxide, but the ignited oxides should be evaporated once or twice with nitric acid to oxidize any reduced tin. Tin may be separated as metal by fusion with potassic cyanide, and phosphoric oxide may be determined after separating tin with sulphydric acid.

22 : 2 : 1 : 2 *Ammonic Stanno-phospho-tungstate.* — When a solution of stanno-chloride of ammonium is poured into a clear cold solution of

24 : 1 sodic phospho-tungstate ($24\ WO_3\ .\ P_2O_5\ .\ 2\ Na_2O + 27$ aq), a beautiful white crystalline precipitate is formed at once. This is but slightly soluble in boiling water. By long boiling with baric chloride, argentic nitrate, or mercurous nitrate, the salt gives crystalline compounds, which in the cases of the barium and silver salts are colorless; in that of the mercurous salt, yellow. So far as can be determined without quantitative analyses, there appears to be in these cases only a simple double decomposition. For analysis the ammonium salt was thoroughly washed with cold water on the filter-pump, drained, and dried on woollen paper. Of this salt,

1.3577 gr. lost on ignition with WO_4Na_2 0.0833 gr.	=	6.14 %	
1.2921 gr. " " without " 0.0812 gr.	=	6.29 %	
1.6822 gr. gave 0.0646 gr. Sn	=	4.88 %	SnO_2
1.1596 gr. " 1.0850 gr. oxides	=	93.57 %	
1.1826 gr. " 0.0443 gr. $P_2O_7Mg_2$	=	2.39 %	
0.9575 gr. " 0.0182 gr $(NH_4)_2O$	=	1.89 %	

The analyses correspond well with the formula

$$22\ WO_3\ .\ 2\ SnO_2\ .\ P_2O_5\ .\ 2\ (NH_4)_2O + 15\ \text{aq},$$

which requires:

22 WO_3	5104	86.21	86.30
2 SnO_2	300	5.06	4.88
P_2O_5	142	2.39	2.39
2 $(NH_4)_2O$	104	1.75	1.89
15 H_2O	270	4.59	4.24
	5920	100.00	99.70

STANNO-PHOSPHO-MOLYBDATES.

The salts of this series are formed under precisely the same conditions as the corresponding stanno-phospho-tungstates. It is at least probable that it will be found that the two classes of salts may be formed under other conditions, as, for example, by boiling stannic oxide with phospho-tungstates and phospho-molybdates, or by digesting stanno-tungstates and stanno-molybdates with alkaline phosphates or with phosphoric acid; but I have made no experiments to determine these points.

Analytical Methods. — Tin may be determined in these salts by fusion with potassic cyanide, provided that, as in the case of the sepa-

ration of antimony from tungsten and from molybdenum, a sufficient quantity of an alkaline carbonate is added to convert all the higher oxides present into neutral salts. Under these circumstances, no insoluble compound of mólybdenum is formed, and the tin separates in bright metallic globules. Phosphoric acid may be determined in these salts after separating the whole of the tin and the greater part of the molybdenum by means of sulphydric acid. Molybdic oxide is estimated most advantageously by difference.

16 : 4 : 3 : 3 *Ammonic Stanno-phospho-molybdate.* — When a solution of stanno-chloride of ammonium, $SnCl_6(NH_4)_2$, is poured into a hot solution of acid ammonic phospho-molybdate,

$$10\ MoO_3 \cdot 2\ P_2O_5 \cdot 5\ (NH_4)_2O + 7\ aq,$$

a fine bright yellow crystalline precipitate is formed, which quickly settles and leaves a colorless solution. The salt is almost insoluble, even in boiling water, and may perhaps find an application in the separation and quantitative estimation of tin. On boiling with mercurous nitrate it gives a buff-yellow crystalline mercurous salt. Under the same circumstances cupric sulphate yields yellowish-green crystals, and argentic nitrate a very pale yellow, not distinctly crystalline salt. An excess of ammonia readily decomposes the salt with separation of a white gelatinous mass. Of this salt,

0.8648 gr.	gave 0.1023 gr. metallic tin	= 15.19 %	SnO_2
2.3780 gr.	" 0.3865 gr. $P_2O_7Mg_2$	= 10.40 %	P_2O_5
1.2021 gr.	" 0.2016 gr. "	= 10.73 %	"
1.0130 gr.	" 0.3839 gr. $(NH_4)_2O$	= 3.79 %	
1.7170 gr.	lost on ignition 0.2793 gr.	= 16.27 %	

The analyses give the formula

$$16\ MoO_3 \cdot 4\ SnO_2 \cdot 3\ P_2O_5 \cdot 3\ (NH_4)_2O + 28\ aq,$$

which requires:

		Calc'd.	Found.	
16 MoO_3	2304	57.75	57.97 (diff.)	
4 SnO_2	600	15.04	15.19	
3 P_2O_5	426	10.67	10.73	10.40
3 $(NH_4)_2O$	156	3.91	3.79	
28 H_2O	504	12.63	12.48	
	3990	100.00		

ALUMINO-MOLYBDATES.

Heinrich Struve,* in 1854, described a remarkable series of salts, which he regarded simply as double molybdates of the sesquioxides of aluminum, iron, manganese, chromium, and ammonia, potash, or soda. These salts were embraced under two different types, particular aluminic, ferric, and chromic salts, having respectively the formulas

$$Al_2O_3 \,.\, 6\, MoO_3 + 3\,(K_2O \,.\, MoO_3) + 20\text{ aq}$$
$$Fe_2O_3 \,.\, 6\, MoO_3 + 3\,(K_2O \,.\, 2\, MoO_3) + 20\text{ aq}$$
$$Cr_2O_3 \,.\, 6\, MoO_3 + 3\,(Na_2O \,.\, 2\, MoO_3) + 21\text{ aq.}$$

The manganic salt, on the other hand, was represented by

$$Mn_2O_3 \,.\, 6\, MoO_3 + 5\,(K_2O \,.\, 2\, MoO_3) + 12\text{ aq.}$$

Parmentier † has recently added a new term to this series, the type being

$$R_2O_3 \,.\, 10\, MoO_3 \,.\, 2\, R'_2O + x\text{ aq.}$$

The true character of these compounds could not be understood at the time of their discovery. I find that in solutions of the salts described by Struve, potassium or ammonium may be directly replaced by other metals or by alkaloids, — a fact which was, however, noticed by Struve himself. In addition, — and this is of more importance, — I find that there are series which contain the sesquioxides named with phosphoric and molybdic oxides, so that we have classes of ferro-phospho-molybdates, etc. From my point of view, the compounds in question may be classed under three types, of which the following will serve as representatives: —

Alumino-dodeka-molybdates,	$Al_2O_3 \,.\, 12\, MoO_3 \,.\, 6\, R_2O$
Ferrico-dodeka-molybdates,	$Fe_2O_3 \,.\, 12\, MoO_3 \,.\, 6\, R_2O$
Chromico-dodeka-molybdates,	$C_2O_3 \,.\, 12\, MoO_2 \,.\, 6\, R_2O$
Manganico-hekkaideka-molybdates,	$Mn_2O_3 \,.\, 16\, MoO_3 \,.\, 5\, K_2O \,.\, H_2O + 11\text{ aq}$
Alumino-deka-molybdates,	$Al_2O_3 \,.\, 10\, MoO_3 \,.\, 2\, R_2O$
Ferrico-deka-molybdates,	$Fe_2O_3 \,.\, 10\, MoO_3 \,.\, 2\, R_2O$
Chromico-deka-molybdates,	$Cr_2O_3 \,.\, 10\, MoO_3 \,.\, 2\, R_2O.$

All these classes of salts containing oxides corresponding to chlorides of the type R_2Cl_6 are very much less stable than compounds containing

* Petersburg Acad. Bull., xii. 142.

† Comptes Rendus, xcv. 839.

oxides of the types R_2O_5, RO_2, and R_2O_3 (corresponding to chlorides RCl_3). We may assume provisionally that the component

$$\begin{array}{l} \mid \\ R = O \\ \mid \\ O \\ \mid \\ R = O \\ \mid \end{array}$$

enters into the structural formulas which represent this class of compounds. Struve states that he has obtained similar compounds containing tungsten, but these have not been described.

Klein * has carefully studied four series of boro-tungstates, embraced respectively under the general formulas

$$\begin{array}{r} 7\ WO_3\ .\ B_2O_3\ .\ 2\ R_2O \\ 9\ WO_3\ .\ B_2O_3\ .\ 2\ R_2O \\ 12\ WO_3\ .\ B_2O_3\ .\ 4\ R_2O \\ 14\ WO_3\ .\ B_2O_3\ .\ 3\ R_2O. \end{array}$$

Since boron is the lowest term in the third column of the periodic series, aluminum being the next higher, it would seem probable that the oxides which correspond to still higher terms in the same column will form similar compounds. Chromium, manganese, iron, nickel, and cobalt may be regarded as higher harmonics of aluminum, and at least three of these form analogous series. It still remains to study the relations of the oxides of the cerium and yttrium groups to molybdic and tungstic oxides, since these correspond to chlorides of the type RCl_3, and yet differ in a very marked degree from oxides like As_2O_3, Sb_2O_3, etc. I have made some progress in this investigation and will in another paper give my results in detail.

GENERAL CONCLUSIONS.

The formulas and details which I have given in the present instalment of my work appear to justify the following general conclusions.

1. Vanadic pentoxide unites with phosphoric or arsenic pentoxides in various proportions to form well-defined complex acids. In some, at least, of these, we seem to have series in which vanadic pentoxide

* Bull. de la Société Chim., [2,] xxxvi. 547, xxxvii. 202.

plays the same part as tungstic or molybdic teroxide, or, in other words, appears to enter the compound as $V_2O_2 . O_3$.

2. Compounds of vanadic pentoxide, vanadic dioxide, and phosphoric or arsenic pentoxide, may be formed, possessing properties analogous to those of the compounds of tungstic or molybdic teroxides with pentoxides and dioxides.

3. The series of oxides P_2O_3, As_2O_3, Sb_2O_3, unite with tungstic and molybdic oxide to form well-defined series of complex acids. In these the ratio of the number of molecules of the oxides of the types R_2O_3 and MO_3 is much lower than in the cases of the compounds which contain orthophosphoric or ortho-arsenic acids.

4. Compounds exist which contain one oxide of the R_2O_3 (or RO_3H_3) and one of the type R'_2O_5 united to tungstic or molybdic oxide, the general formula being

$$m\,MO_3 \,.\, n\,R_2O_3 \,.\, p\,R'_2O_5 \,.\, r\,R''_2O.$$

5. Compounds exist which contain acids of the types RO_2H_3 (hypophosphorous acid, for instance) and R'_2O_5 united to tungstic or molybdic oxides, the general formula being

$$m\,MO_3 \,.\, n\,RO_2H_3 \,.\, p\,R'_2O_5 \,.\, r\,R''_2O.$$

6. Classes of compounds exist which contain oxides of the types RO_2 and R'_2O_5 united to tungstic or molybdic oxides, the general formula being

$$m\,MO_3 \,.\, n\,RO_2 \,.\, p\,R'_2O_5 \,.\, r\,R_2O,$$

where, as in the other general formulas, M represents either tungsten or molybdenum.

7. Compounds exist which contain pyrophosphoric and metaphosphoric acids in place of orthophosphoric acid. So far as it is possible to judge from the salts analyzed, these contain, or at least may contain, phosphoric and tungstic or molybdic oxides in a lower ratio to each other than in the orthophospho-compounds.

8. Complex acids exist which contain two different modifications of phosphoric acid, as, for instance, metaphosphoric and orthophosphoric acids or oxides.

9. The salts described by Struve and by Parmentier establish the existence of a class of complex acids, which contain oxides of the type R_2O_3, corresponding to chlorides of the type R_2Cl_6. The true character of these salts is for the first time recognized.

Partly for convenience of reference, and partly to show as distinctly as possible the extent and richness of the field of investigation now opened, I have collected all the formulas of the last and present instalments of my work, prefixing the mark † to those which are in my judgment less certainly established.

PHOSPHO-VANADATES.

$P_2O_5 . V_2O_5 . (NH_4)_2O + aq.$
$P_2O_5 . V_2O_5 . 2\ Ag_2O + 5\ aq.$
$P_2O_5 . 2\ V_2O_5 . (NH_4)_2O + 7\ aq.$
$4\ P_2O_5 . 6\ V_2O_5 . 3\ K_2O + 21\ aq.$
$7\ P_2O_5 . 6\ V_2O_5 . 3\ H_2O + 34\ aq.$
$20\ V_2O_5 . P_2O_5 . 3\ H_2O + 56\ aq.$

ARSENIO-VANADATES.

$5\ As_2O_5 . 8\ V_2O_5 . 3\ H_2O + 24\ aq.$
† $7\ As_2O_5 . 6\ V_2O_5 . 3\ H_2O.$

PHOSPHO-VANADICO-VANADATES.

$18\ V_2O_5 . VO_2 . 2\ P_2O_5 . 7\ (NH_4)_2O + 50\ aq.$
† $4\ V_2O_5 . VO_2 . 5\ P_2O_5 . 4\ Na_2O + 37\ aq.$
$12\ P_2O_5 . 12\ VO_2 . 6\ V_2O_5 . 5\ K_2O + 40\ aq.$
$12\ P_2O_5 . 14\ VO_2 . 6\ V_2O_5 . 7\ K_2O + 52\ aq.$
$14\ P_2O_5 . 16\ VO_2 . 6\ V_2O_5 . 7\ (NH_4)_2O + 67\ aq.$
$10\ P_2O_5 . 11\ VO_2 . 5\ V_2O_5 . 5\ (NH_4)_2O + 41\ aq.$

ARSENIO-VANADICO-VANADATES.

$12\ As_2O_5 . 12\ VO_2 . 6\ V_2O_5 . 5\ (NH_4)_2O + 7\ aq.$
$9\ As_2O_5 . 9\ VO_2 . 8\ V_2O_5 . 4\ (NH_4)_2O + 11\ aq.$

VANADICO-VANADATES.

$4\ V_2O_5 . 2\ VO_2 . (NH_4)_2O + 8\ aq.$

HYPOPHOSPHO-MOLYBDATES.

$8\ MoO_3 . 2\ PO_2H_3 . 2\ (NH_4)_2O + 2\ H_2O.$

HYPOPHOSPHO-TUNGSTATES.

$18\ WO_3 . 6\ PO_2H_3 . 4\ K_2O + 7\ aq.$

Phosphoroso-molybdates.

$24\ MoO_3 \cdot 4\ PO_3H_3 \cdot 4\ (NH_4)_2O + 17$ aq.
$24\ MoO_3 \cdot 4\ PO_3H_3 \cdot 4\ (NH_4)_2O + 25$ aq.

Phosphoroso-tungstates.

$22\ WO_3 \cdot 4\ PO_3H_3 \cdot 6\ (NH_4)_2O + 25$ aq.
$32\ WO_3 \cdot 16\ PO_3H_3 \cdot 5\ K_2O + 46$ aq.
$22\ WO_3 \cdot 8\ PO_3H_3 \cdot 2\ Na_2O + 25$ aq.

Arsenoso-tungstates.

$18\ WO_3 \cdot 2\ As_2O_3 \cdot 7\ (NH_4)_2O + 18$ aq.
$18\ WO_3 \cdot 2\ As_2O_3 \cdot 8\ BaO + 42$ aq.
$16\ WO_3 \cdot 8\ As_2O_3 \cdot 9\ Na_2O + 65$ aq.

Arsenoso-molybdates.

$8\ MoO_3 \cdot 2\ As_2O_3 \cdot 3\ BaO + 13$ aq.
† $12\ MoO_3 \cdot 5\ As_2O_3 \cdot 3\ (NH_4)_2O + 24$ aq.
$6\ MoO_3 \cdot 3\ As_2O_3 \cdot 2\ MnO + 6$ aq.

Antimonoso-tungstates.

$11\ WO_3 \cdot 3\ Sb_2O_3 \cdot 2\ BaO + 18$ aq.

Antimonoso-molybdates.

$17\ MoO_3 \cdot 3\ Sb_2O_3 \cdot 6\ (NH_4)_2O + 21$ aq.

Phosphoroso-phospho-tungstates.

$24\ WO_3 \cdot P_2O_5 \cdot 2\ PO_3H_3 \cdot 5\ K_2O + 13$ aq.

Phosphoroso-phospho-molybdates.

$72\ MoO_3 \cdot 3\ P_2O_5 \cdot 2\ PO_3H_3 \cdot 9\ (NH_4)_2O + 38$ aq.

Phospho-hypophospho-tungstates.

$26\ WO_3 \cdot 4\ P_2O_5 \cdot 2\ PO_3H_3 \cdot 9\ K_2O \cdot Na_2O + 43$ aq.

Arsenoso-phospho-tungstates.

$32\ WO_3 \cdot 14\ As_2O_3 \cdot 3\ P_2O_5 \cdot 10\ K_2O + 28$ aq.
$12\ WO_3 \cdot 2\ As_2O_3 \cdot 2\ P_2O_5 \cdot 5\ K_2O \cdot Na_2O + 15$ aq.
$60\ WO_3 \cdot As_2O_3 \cdot 4\ P_2O_5 \cdot 7\ K_2O + 55$ aq.

Arsenoso-arsenio-tungstates.

† $21\ WO_3 \,.\, As_2O_3 \,.\, 4\ As_2O_5 \,.\, 10\ K_2O + 26$ aq.

Antimonoso-phospho-tungstates.

$22\ WO_3 \,.\, 5\ Sb_2O_3 \,.\, 6\ P_2O_5 \,.\, 12\ K_2O + 48$ aq.

Vanadio-molybdates.

$6\ MoO_3 \,.\, V_2O_5 \,.\, 2\ (NH_4)_2O + 5$ aq.
$16\ MoO_3 \,.\, 2\ V_2O_5 \,.\, 5\ BaO + 29$ aq.
$18\ MoO_3 \,.\, V_2O_5 \,.\, 8\ (NH_4)_2O + 15$ aq.

Vanadio-tungstates.

$5\ WO_3 \,.\, V_2O_5 \,.\, 4\ (NH_4)_2O + 13$ aq.
$10\ WO_3 \,.\, V_2O_5 \,.\, 6\ H_2O + 16$ aq.
$18\ WO_3 \,.\, V_2O_5 \,.\, 6\ H_2O + 30$ aq.

Antimonio-tungstates.

$12\ WO_3 \,.\, 4\ Sb_2O_5 \,.\, 6\ K_2O + 25$ aq.

Antimonio-molybdates.

$7\ MoO_3 \,.\, 4\ Sb_2O_5 \,.\, 5\ (NH_4)_2O + 12$ aq.

Pyrophospho-tungstates.

$22\ WO_3 \,.\, 9\ P_2O_5 \,.\, 6\ Na_2O \,.\, 14\ (NH_4)_2O + 31$ aq.
$22\ WO_3 \,.\, 9\ P_2O_5 \,.\, 18\ K_2O + 49$ aq.
$22\ WO_3 \,.\, 9\ P_2O_5 \,.\, 13\ K_2O + 49$ aq.

Monometaphospho-tungstates.

† $16\ WO_3 \,.\, 2\ \{PO_3K\}\ 5\ Na_2O + 20$ aq.
$24\ WO_3 \,.\, 2\ \{PO_3K\}\ 3\ K_2O + 20$ aq.
$18\ WO_3 \,.\, 2\ \{PO_3NH_4\}\ (NH_4)_2O + 11$ aq.

Monometaphospho-molybdates.

$10\ MoO_3 \,.\, 4\ \{PO_3NH_4\} \,.\, 3\ (NH_4)_2O + 9$ aq.

Hexametaphospho-molybdates.

† $14\ MoO_3 \,.\, \{Ba_3 \,.\, 6\ PO_3\} \,.\, BaO + 55$ aq.

Orthometaphospho-tungstates.

$22\ WO_3 \,.\, 3\ \{P_2O_5 \,.\, 3\ K_2O\}\ \{6\ PO_3Na\} \,.\, 2\ K_2O \,.\, 2\ Na_2O + 42$ aq.

Phospho-vanadio-molybdates.

$48\ MoO_3 \,.\, 2\ P_2O_5 \,.\, V_2O_5 \,.\, 7\ (NH_4)_2O + 30$ aq.
$14\ MoO_3 \,.\, P_2O_5 \,.\, 8\ V_2O_5 \,.\, 8\ (NH_4)_2O + 50$ aq.

Phospho-vanadio-tungstates.

$60\ WO_3 \,.\, 3\ P_2O_5 \,.\, V_2O_5 \,.\, 10\ (NH_4)_2O + 60$ aq.
$16\ WO_3 \,.\, P_2O_5 \,.\, 3\ V_2O_5 \,.\, 5\ (NH_4)_2O + 37$ aq.
$60\ WO_3 \,.\, 3\ P_2O_5 \,.\, 2\ V_2O_5 \,.\, 18\ BaO + 144$ aq.
$18\ WO_3 \,.\, 3\ P_2O_5 \,.\, 4\ V_2O_5 \,.\, 8\ K_2O + 32$ aq.
† $7\ WO_3 \,.\, P_2O_5 \,.\, V_2O_5 \,.\, 3\ K_2O + 11$ aq.

Vanadico-vanadio-molybdates.

$28\ MoO_3 \,.\, VO_2 \,.\, 4\ V_2O_5 \,.\, 11\ (NH_4)_2O + 20$ aq.
$30\ MoO_3 \,.\, 3\ VO_2 \,.\, 2\ V_2O_5 \,.\, 14\ BaO + 48$ aq.

Vanadico-vanadio-tungstates.

$12\ WO_3 \,.\, 3\ VO_2 \,.\, 2\ V_2O_5 \,.\, 6\ Na_2O + 43$ aq.
$12\ WO_3 \,.\, 3\ VO_2 \,.\, 2\ V_2O_5 \,.\, 6\ (NH_4)_2O + 12$ aq.
$12\ WO_3 \,.\, 3\ VO_2 \,.\, 2\ V_2O_5 \,.\, 6\ Ag_2O + 8$ aq.

Stanno-phospho-molybdates.

$16\ MoO_3 \,.\, 4\ SnO_2 \,.\, 3\ P_2O_5 \,.\, 3\ (NH_4)_2O + 28$ aq.

Stanno-phospho-tungstates.

$22\ WO_3 \,.\, 2\ SnO_2 \,.\, P_2O_5 \,.\, 2\ (NH_4)_2O + 15$ aq.

Phospho-vanadio-vanadico-tungstates.

$60\ WO_2 \,.\, 3\ P_2O_5 \,.\, V_2O_5 \,.\, VO_2 \,.\, 18\ BaO + 15$ aq.

To these I will add the new formulas of the salts described by Struve and Parmentier : —

Struve's Salts.

$Al_2O_3 . 12 MoO_3 . 6 K_2O + 20$ aq.
$Al_2O_3 . 12 MoO_3 . 6 (NH_4)_2O + 20$ aq.
$Al_2O_3 . 12 MoO_3 . 6 Na_2O + 22$ aq.*
$Fe_2O_3 . 12 MoO_3 . 6 K_2O + 20$ aq.
$Fe_2O_3 . 12 MoO_3 . 6 (NH_4)_2O + 20$ aq.
$Cr_2O_3 . 12 MoO_3 . 6 K_2O + 20$ aq.
$Cr_2O_3 . 12 MoO_3 . 6 (NH_4)_2O + 20$ aq.
$Cr_2O_3 . 12 MoO_3 . 6 Na_2O + 21$ aq.
$Mn_2O_3 . 16 MoO_3 . 5 K_2O + 12$ aq.
$Mn_2O_3 . 16 MoO_3 . 5 (NH_4)_2O + 12$ aq.

Parmentier's Salts.

$Al_2O_3 . 10 MoO_3 . 2 K_2O + 15$ aq.
$Fe_2O_3 . 10 MoO_3 . 2 K_2O + 15$ aq.?
$Cr_2O_3 . 10 MoO_3 . 2 K_2O + 15$ aq.?

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* Gentele, Journal für prakt. Chemie, lxxxi. 413.

Cambridge, July 8, 1885.

(To be continued.)